

Handwritten: JUL 19 1995

ENGINEERING DATA TRANSMITTAL

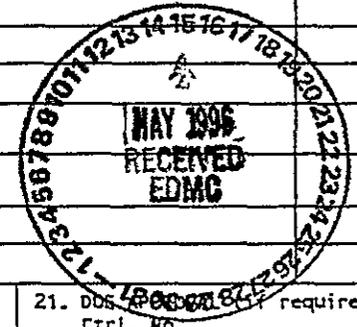
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2. To: (Receiving Organization) TWRS Compliance Plans	3. From: (Originating Organization) Process Engineering	4. Related EDT No.: 608730
5. Proj./Prog./Dept./Div.: Tank Waste Remediation System	6. Cog. Engr.: A. L. Boldt	7. Purchase Order No.: n/a
8. Originator Remarks: This engineering data package provides supporting data for preparation of the TWRS Environmental Impact Statement. Data in this document summarize technical options for treatment and disposal of Hanford tank waste that have been previously identified and rejected. Environmental, Safety, and QA approvals required by WHC-CM-3-5 Section 12.7 were obtained on Rev. B of this document (EDT 608730). Information in Rev. 0 of this document has not changed from the earlier Rev. B of this document.		9. Equip./Component No.: n/a
11. Receiver Remarks:		10. System/Bldg./Facility: n/a
		12. Major Assm. Dwg. No.: n/a
		13. Permit/Permit Application No.: n/a
		14. Required Response Date: n/a

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(A) Item No.	(B) Document/Drawing No.	(C) Sheet No.	(D) Rev. No.	(E) Title or Description of Data Transmitted	Approval Designator	Reason for Transmittal	Originator Disposition	Receiver Disposition
1	WHC-SD-WM-EV-106		0	Other Options Data Package for the Tank Waste Remediation System Environmental Impact Statement	E/S/Q	2	1	1

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

17. SIGNATURE/DISTRIBUTION (See Approval Designator for required signatures)											
(G) Reason	(H) Disp.	(J) Name	(K) Signature	(L) Date	(M) MSIN	(J) Name	(K) Signature	(L) Date	(M) MSIN	(G) Reason	(H) Disp.
	2	1	Cog. Eng. A. L. Boldt	<i>[Signature]</i>	7/14/95						
	2	1	Cog. Mgr. J. P. Slaughter	<i>[Signature]</i>	7-14-95						
			QA (approved by J. Weber, on EDT 608730)	<i>[Signature]</i>	page 2 of this EDT						
			Safety (approved by J. M. Garcia, on EDT 608730)	<i>[Signature]</i>	page 2 of this EDT						
			Env. (approved by R. H. Engelmann, on EDT 608730)	<i>[Signature]</i>	page 2 of this EDT						



18. A. L. Boldt <i>[Signature]</i> 7/14/95 Signature of EDT Originator Date	19. <i>[Signature]</i> E. E. Borneman 7/18/95 Authorized Representative Date for Receiving Organization	20. <i>[Signature]</i> J. P. Slaughter 7-14-95 Cognizant Manager Date	21. Does Approval (EDT required) Ctrl. No. <input type="checkbox"/> Approved <input type="checkbox"/> Approved w/comments <input type="checkbox"/> Disapproved w/comments <input checked="" type="checkbox"/> Not Required per Waiver WA-557
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ENGINEERING DATA TRANSMITTAL

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5. Proj./Prog./Dept./Div.: TWRS	6. Cog. Engr.: A. L. Boldt	7. Purchase Order No.: na
8. Originator Remarks: This engineering data package provides the supporting data for the "Other Options" to be used in the preparation of the TWRS Environmental Impact Statement (EIS). This EDT transmits the data package to TWRS Compliance Plans as Rev. B, for DOE-RL approval, per WHC-CM-3-5, Section 12.7.		9. Equip./Component No.: na
		10. System/Bldg./Facility: na
11. Receiver Remarks:		12. Major Assm. Dwg. No.: na
		13. Permit/Permit Application No.: na
		14. Required Response Date:

15. DATA TRANSMITTED					(F)	(G)	(H)	(I)
(A) Item No.	(B) Document/Drawing No.	(C) Sheet No.	(D) Rev. No.	(E) Title or Description of Data Transmitted	Approval Designator	Reason for Transmittal	Originator Disposition	Receiver Disposition
1	WHC-SD-WM-EV-106		B	Other Options Data Package for the Tank Waste Remediation System Environmental Impact Statement	ESQ	1	1	
					D	4	LEB waver on file	

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

17. SIGNATURE/DISTRIBUTION (See Approval Designator for required signatures)											
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1	/	Cog. Eng. A.L. Boldt	<i>A.L. Boldt</i>	3/16/95	45-19						
1	/	QA J. Weber	<i>J. Weber</i>	3/14/95							
1	/	Safety J.M. Garcia	<i>J.M. Garcia</i>	3/15/95							
1	/	Eng. R.F. Engel	<i>R.F. Engel</i>	3-16-95							
1	/	E. Borneman	<i>E. Borneman</i>	3/16/95							
1	/	J.O. Honeyman	<i>J.O. Honeyman</i>								

18. A.L. Boldt Signature of EDT Originator <i>A.L. Boldt</i> 3/16/95	19. L.E. Borneman Authorized Representative for Receiving Organization <i>L.E. Borneman</i> 3/16/95	20. <i>A.L. Boldt</i> Cognizant Manager Date 3/16/95	21. DOE APPROVAL (if required) Ctrl. No. <input type="checkbox"/> Approved <input type="checkbox"/> Approved w/comments <input type="checkbox"/> Disapproved w/comments
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RELEASE AUTHORIZATION

Document Number: WHC-SD-WM-EV-106, REV 0

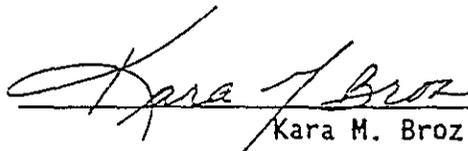
Document Title: Other Options Data Package for the Tank Waste
Remediation System Environmental Impact Statement

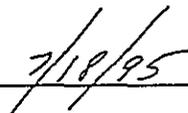
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Kara M. Broz


7/18/95

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SUPPORTING DOCUMENT

1. Total Pages 179

2. Title

Other Options Data Package for the Tank Waste Remediation System Environmental Impact Statement

3. Number

WHC-SD-WM-EV-106

4. Rev No.

0

5. Key Words

other options, waste treatment, separations, onsite disposal, offsite disposal, environmental impact statement, NEPA

6. Author

Name: A. L. Boldt

Signature

Organization/Charge Code 74D00/D1DDB

7. Abstract

This engineering data package summarizes technical options for treatment and disposal of Hanford tank waste that have been previously identified and rejected for further evaluation, and are therefore not addressed in the TWRS Environmental Impact Statement.

8. RELEASE STAMP

OFFICIAL RELEASE
BY WHC
DATE JUL 19 1995
He 4

Other Options Data Package for the Tank Waste Remediation System Environmental Impact Statement

A. L. Boldt

Date Published
July 1995

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



Westinghouse
Hanford Company

P.O. Box 1970
Richland, Washington

Management and Operations Contractor for the U.S. Department
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Approved for Public Release

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1.0 INTRODUCTION

Technology options previously identified and rejected for further evaluation are not evaluated in the Tank Waste Remediation System (TWRS) Environmental Impact Statement (EIS) data packages. This report is a data package of extracts from historical source documents provided to Jacobs Engineering for preparation of the other alternatives section(s) of the TWRS EIS. Options were identified and rejected by either the National High-Level Waste (HLW) Disposal Program or Westinghouse Hanford Company (WHC). The rejected disposal options, rejected HLW forms, rejected methods of radionuclide removal, and other technical options are listed below:

1.1 DISPOSAL OPTIONS

The Office of Technology Assessment evaluated disposal options (OTA, 1985) and rejected the following options in favor of geologic disposal in an engineered geologic repository.

- Subseabed
- Deep holes
- Rock melting
- Well injection
- Ice sheets
- Space
- Transmutation

1.2 HIGH-LEVEL WASTE FORMS

The National Research Council evaluated HLW forms (NRC, 1983) and rejected the following waste forms in favor of borosilicate glass.

- Sintered high-silica glass
- Concrete (FUETAP)
- Calcines
- Clay ceramics
- SYNROC
- Glass ceramic
- Sol-gel ceramics
- Metal matrix
- Concrete or ceramic matrices
- Multibarrier materials.

1.3 RADIONUCLIDE REMOVAL

An analysis of the impact of not removing hydrogen-3 (tritium), carbon-14 and iodine-129 indicates the maximum offsite individual will receive a 50-year dose commitment from atmospheric releases of less than 0.7 mrem/yr (Appendix A, Letter, J. M. Colby to J. S. Garfield). This is 0.2 percent of the national average individual dose from background of 300 mrem/yr. As a result of this analysis, removal of hydrogen-3 (tritium), carbon-14 and iodine-129 from the low-level waste (LLW) feed was not considered in the EIS data packages rejected.

1.4 OTHER TECHNICAL OPTIONS

Boomer et al., 1993, *Tank Waste Technical Options Report*, provides the basis for selecting the EIS options. The report describes technology options that were and options that were not evaluated in engineering studies. Data used in the *Tank Waste Technical Options Report* are appended to this report as follows:

Retrieval - Appendix B

- Selection of Retrieval Technology Options
- Waste Retrieval Options
- Technology Selection
- Retrieval and Transfer Function Elements
- References

Separations (Pretreatment) - Appendix C

- Selection of Separations Technology Options
- Selection of Separations Technology Options
- References

Waste Treatment for Onsite Disposal (LLW) - Appendix D

- Technical Option Selection
- Technical Option Selection
- References

Waste Treatment for Offsite Disposal (HLW) - Appendix E

- Technical Option Selection
- Waste Form
- References

The appendices to the *Tank Waste Technical Options Report*, from which most of the information in Appendices B through E was extracted, were never released to the public. Consequently information in these appendices has not been subjected to a level of review appropriate for external or public release. Also, information in these appendices has not been updated to reflect changes since 1993. The following corrections and clarifications address known errors; and misleading, incomplete, or outdated information in Appendices B through E that were identified during the Westinghouse Hanford Company internal review of this data package. None of these corrections and clarifications would have affected the conclusions reached in the *Tank Waste Technical Options Report*.

Appendix B

Page B-17, Section 6.3.1.3: Leaks from single-shell tanks during sluicing would require notification of regulatory authorities and mitigation and control in accordance with Washington Administrative Code (WAC) regulations governing treatment, storage, and disposal of dangerous waste, and with any permits covering such regulated activities. Remediation, if required, of contaminated soil resulting from past leaks, and from new leaks during sluicing operations is planned to be conducted in accordance with a closure plan and/or waste disposal plan for the single-shell tank farms approved by the state and federal regulatory authorities having jurisdiction. This strategy has not yet been approved by the regulatory authorities.

Page B-20, Section F3.2.2.1: The January 1994 amendment to the Tri-Party Agreement changed the milestones and schedules cited in this section.

Page B-33, Section F10.0, References: DOE, 1986, *Draft Environmental Impact Statement - Disposal of Hanford Defense High-Level, Transuranic and Tank Wastes* was replaced by *Final Environmental Impact Statement - Disposal of Hanford Defense High-Level, Transuranic and Tank Wastes*, December, 1987. The earlier draft is included in the Section F10.0 references because it contained information relevant to this appendix to the *Tank Waste Technical Options Report* that was not included in the final Environmental Impact Statement.

Appendix C

Page C-5/C-6, Figure 7-2, Sheet 1 of 2, and page C-32, paragraph f, Nickel Ferrocyanide Precipitation of ¹³⁷Cs: Ferrocyanide has aged in the tanks so that it is no longer considered a safety issue.

Page C-7/C-8, Figure 7-2, Sheet 2 of 2: The "x" (referring to Crown Ether in Normal Paraffin Hydrocarbon) adjacent to the block entitled "Molecular Recognition" should be deleted. An "x" should be added adjacent to the block entitled "Crown Ether."

Page C-9, Section 7.1.1.2, Strontium 90: In last sentence in paragraph, NHO₃ should be HNO₃.

Page C-27, Section G.1.1.3: In the first paragraph at the top of the page, "ethylenediaminetriacetic acid [HEDTA]" should be "ethylenediaminetriacetic acid [EDTA]".

Page C-38, Section v. Steam Reforming: In the first paragraph at the top of the page, "stream reforming" should be "steam reforming".

Page C-46, Section kk. Cobalt Dicarbollide: One reviewer of this data package commented that sufficient justification had not been provided to characterize the cobalt dicarbollide extraction process as having overriding technical disadvantage, based on concerns over toxicity or corrosivity of cobalt dicarbollide extractant.

2.0 REFERENCES

- Boomer, K.D., S. K. Baker, A. L. Boldt, J. D. Galbraith, J. S. Garfield, C. E. Golberg, B. A. Higley L. J. Johnson, M. J. Kupfer, R. M. Marusich, R. J. Parazin, A. N. Praga, G. W. Reddick, E. J. Slaathaug, L. M. Swanson, T. L. Waldo, C. E. Worcester, 1993, *Tank Waste Technical Options Report*, WHC-EP-0616, Rev 0, Westinghouse Hanford Company, Richland, Washington.
- Colby, J. M. Letter to J. S. Garfield, July 27, 1994, "Preliminary Offsite Dose Calculations for TWRS Activities," Westinghouse Hanford Company, Richland, Washington.
- NRC, 1983, *A Study of the Isolation System for Geologic Disposal of Radioactive Wastes*, Waste Isolation Systems Panel, Board on Radioactive Waste Management, National Research Council, National Academy Press.
- OTA, 1985, *Managing the Nation's Commercial High-Level Radioactive Waste*, Office of Technology Assessment.

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APPENDIX A

LETTER FROM J. M. COLBY TO J. S. GARFIELD

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**Westinghouse
Hanford Company**

**Internal
Memo**

From: TWRS Process Design 7E330-94-018
 Phone: 376-3686
 Date: July 27, 1994
 Subject: PRELIMINARY OFFSITE DOSE CALCULATIONS FOR TWRS ACTIVITIES

To: J. S. Garfield H5-49
 cc: A. L. Boldt H5-49
 K. D. Boomer H5-49
 C. E. Leach H5-49
 JMC:JSG File/LB H5-49

- References: (1) Article, NCRP, "Exposure of the Population in the United States and Canada from Natural Background Radiation;" Recommendations of the National Council on Radiation Protection and Measurements, Publication 94, Page 148, National Council on Radiation Protection, Bethesda, Maryland, 1987.
- (2) DSI, A. L. Boldt, to K. D. Boomer, "Source Terms," February 9, 1994.
- (3) DOE-RL-92-41, Radioactive Air Emissions Notice of Construction and Application for Approval to Construct the Hanford Waste Vitrification Plant, Revision 0, U.S. Department of Energy-Richland Operations Office, Richland, Washington, 1992.
- (4) Parks, B. S., User's Guide for CAP88-PC, Version 1.0, United States Environmental Protection Agency, Las Vegas, Nevada, 1992.
- (5) Book, Napier, B. A., R. A. Peloquin, D. L. Strenge, and J. V. Ramsdell, GENII - The Hanford Environmental Radiation Dosimetry Software System, PNL-6584, Vols. 1-3, Pacific Northwest Laboratory, Richland, Washington, 1988.

Preliminary dose calculations were performed in support of the Tank Waste Remediation System (TWRS) Facility Configuration Study. The results of the calculations are presented in the Table 1. As shown in the table the total dose resulting from tritium (^3H), carbon-14 (^{14}C), and iodine-129 (^{129}I) during routine operations is 0.7 mrem/yr, based on the CAP88 computer code. This is less than the annual dose received from natural background radiation for a person living in the United States or Canada (300 mrem/yr) (Reference 1).

Radionuclides in the source term were provided in a DSI (memo) from A. L. Boldt to K. D. Boomer (Reference 2). The dose values were calculated using "Unit Dose Calculations for Routine Radionuclide Releases from the

J. S. Garfield
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 July 27, 1994

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Hanford Waste Vitrification Project" (Reference 3). A copy of Appendix 2B, of DOE/RL-92-41, Revision 0, Radioactive Air Emissions Notice of Construction and Application for Approval to Construct the Hanford Waste Vitrification Plant, (Reference 3), is attached. The total dose expected from air emissions (0.7 mrem/yr) was calculated by multiplying the release quantity in curies for each radionuclide by the corresponding unit dose factor and adding the contributions for the nuclides in the effluent stream. Since the primary dose contributors are ³H, ¹⁴C, and ¹²⁹I, doses were calculated only for these radionuclides.

Doses were calculated as 50-year committed effective dose equivalents for all internal deposition pathways using both the CAP88-PC (Reference 4) and the GENII (Reference 5) computer packages, resulting in doses of 0.7 and 0.26 mrem/yr, respectively. For additional information on the CAP88-PC and GENII computer packages, see the attachment to this letter. The location of the maximally exposed individual is 16 km east of the 200 East Area Plateau. This location is based on the site boundary location having the greatest radionuclide air concentration under average atmospheric conditions. Finally, the dose calculations were based on a 67-m stack with momentum plume rise. This is intended to represent emissions from Zone I areas of the facility (i.e., the melter), which is the primary contributor to the total dose received by the maximally exposed individual.

Table 1

Preliminary Dose Calculations for Tank Waste Remediation System Activities
 50-Year Committed Effective Dose Equivalent for All Internal Deposition Pathways; Maximally Exposed Individual: 16 km East.

Radionuclide	Curies to Separations	67-m stack momentum plume rise		Dose	
		(GENII) mrem/Ci	(CAP88) mrem/Ci	(GENII) mrem	(CAP88) mrem
³ H	3.0 E+03	4.2 E-06	8.0 E-06	1.3 E-02	2.4 E-02
¹⁴ C	5.3 E+03	8.7 E-04	4.4 E-04	4.6 E+00	2.3 E+00
¹²⁹ I	5.1 E+01	1.7 E-01	6.5 E-01	8.7 E+00	3.3 E+01
Total (mrem)				1.3 E+01	3.5 E+01
Total (mrem/yr)				2.6 E-01	7.0 E-01

J. S. Garfield
Page 3
July 27, 1994

7E330-94-018

If you have any questions regarding the information presented in this letter, you may contact me at 376-3686 or you may contact Al Boldt at 376-1003.

J. M. Colby
Advanced Engineer

hmr

Attachments 5

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APPENDIX 28

UNIT DOSE CALCULATIONS FOR HANFORD WASTE VITRIFICATION PROJECT

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14	CAP88-PC DOSE MODELING INPUT FILES APP 28-31
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16	GENII DOSE MODELING INPUT FILES APP 28-65
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DOE/RL-92-41, Rev. 0
09/25/92UNIT DOSE CALCULATIONS FOR ROUTINE RADIONUCLIDE RELEASES FROM HANFORD WASTE
VITRIFICATION PROJECT

L. H. Sawyer

June 11, 1992

INTRODUCTION

Dose calculations for unit (1 Ci) radionuclide releases were performed in support of the Westinghouse Hanford Company (WHC) air permitting activities for the Hanford Waste Vitrification Project (HWVP). Atmospheric releases from the 200 E area were modeled for elevated releases using effective stack height, and plume rise by both momentum and buoyancy. Both the CAP88-PC (Parks 1992) and GENII (Napier et al. 1988) computer packages were used to model atmospheric releases in order to satisfy requirements of the U.S. Environmental Protection Agency (USEPA 1989) and Hanford Dose Overview Panel.

METHODS

Radionuclides in the source term were provided in a DSI from J. M. Ring (Attachment 1). Standard parameters for Hanford dose calculations were included in the calculations where possible (McCormack, et al 1984). Meteorology data were collected at the 200 area weather station at 10 m for CAP88-PC and 61 m for GENII. These data represent the five-year averages of values taken between 1983 and 1987. The location of the maximally exposed individual (MI) is listed in attached tables with the dose calculations. The location of the MI was based on the site boundary location having the greatest radionuclide air concentration (i.e. the location having the highest Chi/Q value) under average atmospheric conditions (see Attachment 2, Table 1). Doses were calculated as 50-year committed effective dose equivalents for all internal deposition pathways using the EPA model specified in 40 CFR 61. Default solubility classes were used for all radionuclides in these generic unit Ci calculations. These should be appropriate for most facilities evaluated, except where plutonium or uranium are released in soluble form and contribute substantially to the overall dose from the facility. Default classes for uranium and plutonium assume these radionuclides are released as insoluble compounds; this will result in a lower overall dose than would be the case if they were released in more soluble form.

RESULTS

Results of the evaluations are presented in Tables 2 and 3, Attachment 3, and represent the 50-year committed dose equivalent following a chronic annual release of 1 Ci of each radionuclide. The CAP88-PC and GENII codes handle ingrowth of long-lived radioactive decay products differently, as noted in the tables. GENII calculates doses for all radionuclides in each decay chain, therefore, the doses reported in Table 2 include contributions from both parent and ingrown decay products. CAP88-PC does not calculate activities for ingrowth of progeny radionuclides following the release of the parent, but will estimate the dose from very short-lived progeny where the parent-to-progeny activity ratio is effectively 1:1. CAP88-PC doses reported in Table 3 are adjusted to reflect the dose from the parent radionuclide plus ingrown progeny. CAP88-PC parental doses were divided by the fractional contribution from the parent nuclide reported in the GENII results to get the total dose from parents and progeny.

The total dose expected from emissions can be obtained by multiplying the release quantity in Ci for each radionuclide by the corresponding unit-dose

APP 2B-1

DOE/RL-92-41, Rev. 0
09/25/92

factor in the tables, and summing the contributions for all nuclides in the effluent stream. Please note that doses calculated using the GENII code are reported as rem to the HI from an annual release; those from CAP88-PC are reported in mrem. Values in the tables were manipulated from code outputs, and have been left in the units reported by each code to avoid transcription errors.

REFERENCES

McCormack, W. D., J. V. Ramsdell, and B. A. Napier. 1984. Hanford Dose Overview Program: Standardized Methods and Data for Hanford Environmental Dose Calculations. PNL-3777, Rev. 1, Pacific Northwest Laboratory, Richland, Washington.

Napier, B. A., R. A. Peloquin, D. L. Strenge, and J. V. Ramsdell. 1988. GENII - The Hanford Environmental Radiation Dosimetry Software System. PNL-6584, Vols. 1-3. Pacific Northwest Laboratory, Richland, Washington.

Parks, B. S. 1992. Users's Guide for CAP88-PC, Version 1.0. United States Environmental Protection Agency, Las Vegas, Nevada.

U.S. Environmental Protection Agency. 1989. National Emission Standards for Hazardous Air Pollutants: Radionuclides; Final Rule and Notice of Reconsideration. 40 CFR Part 61, Federal Register 54 (240):51654-51715.

HEDOP REVIEW CHECKLIST
for
Radiological and Nonradiological Release Calculations

Document reviewed (include title or description of calculation, document number, author, and date, as applicable):

Unit Dose Calculations for Hanford Waste Vitrification Project

Submitted by: Lissa Sawyer

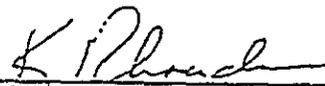
Date Submitted: 6/11/92

Scope of Review:

- | YES | NO* | N/A | |
|-------------------------------------|--------------------------|-------------------------------------|--|
| <input checked="" type="checkbox"/> | <input type="checkbox"/> | <input type="checkbox"/> | 1. A detailed technical review and approval of the environmental transport and dose calculation portion of the analysis has been performed and documented. |
| <input type="checkbox"/> | <input type="checkbox"/> | <input checked="" type="checkbox"/> | 2. Detailed technical review(s) and approval(s) of scenario and release determinations have been performed and documented. |
| <input checked="" type="checkbox"/> | <input type="checkbox"/> | <input type="checkbox"/> | 3. HEDOP-approved code(s) were used. |
| <input type="checkbox"/> | <input type="checkbox"/> | <input checked="" type="checkbox"/> | 4. Receptor locations were selected according to HEDOP recommendations. |
| <input checked="" type="checkbox"/> | <input type="checkbox"/> | <input type="checkbox"/> | 5. All applicable environmental pathways and code options were included and are appropriate for the calculations. |
| <input checked="" type="checkbox"/> | <input type="checkbox"/> | <input type="checkbox"/> | 6. Hanford site data were used. |
| <input type="checkbox"/> | <input type="checkbox"/> | <input checked="" type="checkbox"/> | 7. Model adjustments external to the computer program were justified and performed correctly. |
| <input checked="" type="checkbox"/> | <input type="checkbox"/> | <input type="checkbox"/> | 8. The analysis is consistent with HEDOP recommendations. |
| <input type="checkbox"/> | <input type="checkbox"/> | <input checked="" type="checkbox"/> | 9. Supporting notes, calculations, comments, comment resolutions, or other information is attached. (Use the "Page 1 of X" page numbering format and sign and date each added page.) |
| <input checked="" type="checkbox"/> | <input type="checkbox"/> | <input type="checkbox"/> | 10. Approval is granted on behalf of the Hanford Environmental Dose Overview Panel. |

* All "NO" responses must be explained and use of nonstandard methods justified.

Kathy Rhoads



HEDOP-Approved Reviewer (Printed Name and Signature)

6/12/92

Date

COMMENTS (add additional signed and dated pages if necessary):

CHECKLIST FOR CALCULATION REVIEW

DOE/RL-92-41, Rev. 0
09/25/92

Document Reviewed:

Scope of Review:

- | Yes | No | N/A | |
|-------------------------------------|-------------------------------------|-------------------------------------|--|
| <input type="checkbox"/> | <input type="checkbox"/> | <input checked="" type="checkbox"/> | Previous reviews complete and cover analysis, up to scope of this review; with no gaps. |
| <input checked="" type="checkbox"/> | <input type="checkbox"/> | <input type="checkbox"/> | Problem completely defined. |
| <input checked="" type="checkbox"/> | <input type="checkbox"/> | <input type="checkbox"/> | Necessary assumptions explicitly stated and supported. |
| <input checked="" type="checkbox"/> | <input type="checkbox"/> | <input type="checkbox"/> | Computer codes and data files documented. |
| <input checked="" type="checkbox"/> | <input type="checkbox"/> | <input type="checkbox"/> | Data used in calculations explicitly stated in document. |
| <input checked="" type="checkbox"/> | <input type="checkbox"/> | <input type="checkbox"/> | Data checked for consistency with original source information as applicable. |
| <input type="checkbox"/> | <input type="checkbox"/> | <input checked="" type="checkbox"/> | Mathematical derivations checked including dimensional consistency of results. |
| <input checked="" type="checkbox"/> | <input type="checkbox"/> | <input type="checkbox"/> | Models appropriate and used within range of validity or use outside range of established validity justified. |
| <input checked="" type="checkbox"/> | <input type="checkbox"/> | <input type="checkbox"/> | Hand calculations checked for errors. Spreadsheet results should be treated exactly the same as hand calculations. |
| <input checked="" type="checkbox"/> | <input type="checkbox"/> | <input type="checkbox"/> | Code runstreams correct and consistent with analysis documentation. |
| <input checked="" type="checkbox"/> | <input type="checkbox"/> | <input type="checkbox"/> | Code output consistent with input and with results reported in analysis documentation. |
| <input type="checkbox"/> | <input type="checkbox"/> | <input checked="" type="checkbox"/> | Acceptability limits on analytical results applicable and supported. Limits checked against sources. |
| <input type="checkbox"/> | <input type="checkbox"/> | <input checked="" type="checkbox"/> | Safety margins consistent with good engineering practices. |
| <input checked="" type="checkbox"/> | <input type="checkbox"/> | <input type="checkbox"/> | Conclusions consistent with analytical results and applicable limits. |
| <input checked="" type="checkbox"/> | <input type="checkbox"/> | <input type="checkbox"/> | Results and conclusions address all points required in the problem statement. |
| <input type="checkbox"/> | <input checked="" type="checkbox"/> | <input type="checkbox"/> | * Review calculations, comments, and/or notes are attached. |

Kathy Rhoads K Rhoads 6/12/92
 Reviewer Approval (Printed Name and Signature) Date

HEDOP Review (Radiological and Toxicological Release Calculations)

- | | | | |
|-------------------------------------|-------------------------------------|--------------------------|--|
| <input checked="" type="checkbox"/> | <input type="checkbox"/> | <input type="checkbox"/> | GENII (current version) used for radiological calculations. |
| <input checked="" type="checkbox"/> | <input type="checkbox"/> | <input type="checkbox"/> | Appropriate receptor locations evaluated. |
| <input checked="" type="checkbox"/> | <input type="checkbox"/> | <input type="checkbox"/> | Appropriate models (finite plume vs. semi-infinite cloud, building wake, etc.) used. |
| <input checked="" type="checkbox"/> | <input type="checkbox"/> | <input type="checkbox"/> | Appropriate pathways evaluated for each receptor. |
| <input checked="" type="checkbox"/> | <input type="checkbox"/> | <input type="checkbox"/> | Analysis consistent with HEDOP Recommendations. |
| <input type="checkbox"/> | <input checked="" type="checkbox"/> | <input type="checkbox"/> | * Review calculations, comments, and/or notes are attached. |

Kathy Rhoads K Rhoads 6/12/92
 HEDOP Reviewer Approval (Printed Name and Signature) Date

* Any calculations, comments, or notes generated as part of this review should be signed, dated and attached to this checklist. Such material should be labeled and recorded in such a manner as to be intelligible to a technically qualified third party.

APPLICATION REPORT

1) Project title and number Hanford Waste Vitrification Program FD2505

2) Purpose of application package and relationship to other work:

Revised Environmental Compliance radiation dose calculations for Hanford Waste Vitrification Plant. Calculations are for the maximally exposed individual using the CAP88 and GENII computer code packages. Calculations are made with chronic unit Ci releases from the Vitrification facility.

3) List original sources of input data, assumptions and derivations used to obtain it, and justification for its use, as appropriate. (If input information has been previously reviewed, reference the documentation of this review.)

Input data are documented in the following letter report:
L. H. Sawyer to J. M. Ring June 11, 1992, "Unit Dose Calculations for Routine Radionuclide Releases from Hanford Waste Vitrification Project."

4) Minor changes made in the software that produced the application run (see Section 4.1). N/A

5) Describe interrelationships and dependencies of each application run in the application package:

Calculations were made for the maximally exposed individual using unit Ci chronic releases with the GENII and CAP88-PC computer software packages. Doses due to secondary members of decay chains were calculated by two methods. First, the dose from ingrown progeny were added into the dose from the parent and were reported in the value for the parent. Additionally, the dose from the unit Ci dose release of the progeny was reported separately for the progeny. In cases where CAP88-PC did not include progeny, but GENII did, the CAP88-PC values were adjusted to reflect the dose from ingrowth of progeny. The parental dose calculated by CAP88-PC was divided by the GENII derived percent dose from parent. The resulting value reflected the total estimated dose from the release of the parent radionuclide with ingrowth of progeny.

6) Summarize the overall output of the application package in relation to the purpose stated in item 2 above (including tables and graphs, as appropriate):

Results are summarized in the letter report referred to in section 3.

7) Submitted to the Hanford Dose Overview Panel for review by:
Lissa Sawyer [Signature] June 11, 1992
Preparer Date

8) Approved for the Hanford Dose Overview Panel by:
K. Rhoads (Kathy Rhoads) 6/12/92
Reviewer Date

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LIST OF ATTACHMENTS

- Attachment 1. DSI from JM Ring to K Rhoads. Statement of Work
- Attachment 2. Chi/Q Information
- Table 1. Distance from 200 E Area to Site Boundary and Associated Chi/Q.
- Attachment 3. Tables of Dose Analysis results
- Table 2. GENII Dose Conversion Factors
- Table 3. CAP88-PC Dose Conversion Factors
- Attachment 4. Application Record Log

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ATTACHMENT 1.

DSI from JH Ring to K Rhoads. Statement of Work.

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APP 2B-10

DOE/RL-92-41, Rev. 0
09/25/92

81173-92-DSI-013

DOH'T SAY IT --- Write It!

DATE: March 13, 1992

TO: K. Rhoads K3-54

FROM: J. M. Ring H4-57

Telephone: 6-8162

cc: D. G. Baide G6-16
J. M. Colby G6-16
J. H. LaRue G6-16
JMR/File/LB H4-57

SUBJECT: STATEMENT OF WORK FOR WORK ORDER ED2505

The following is provided as a description of work to be performed by Pacific Northwest Laboratories (PNL) under work order number ED2505.

PNL will provide offsite dose calculations for one-curie atmospheric releases of each of the radionuclides expected to be emitted from HWVP. (See list at end of DSI.) The calculations will be used to support the development of control technology assessments and other documentation to be submitted to the regulatory authorities pursuant to 40 CFR 61 and WAC 246-247.

Unit curie releases of each of the radionuclides expected from HWVP, located in the Hanford Site 200 East Area, will be modeled using both the CAP-88 and GENII code packages. The modeling activities should use Hanford Site-specific meteorological data and should calculate potential effective dose equivalent to the theoretical maximally exposed offsite individual at 16 kilometers east of the 200E Area (Ringold).

Three separate dose calculations will be generated. The first calculation should assume release of the radionuclides from a 200 ft/61 m stack height, with the effective stack height equal to the actual stack height; i.e., no plume rise modeling will be necessary for this first run. The second and third calculations will be performed for two separate HWVP stacks, using stack-specific data and plume rise modeling. The following information is necessary to develop the second and third sets of calculations.

Stack Variable	Vit Bldg Zone I Stack	Vit Bldg Zone II and III Stack
Stack height	219 feet	195 feet
Stack diameter (ID)	7 feet	10 feet
Exhaust gas temperature	104°F	104°F
Gas exit velocity	97,500 SCFH; 108,708 ACFH	220,875 SCFH; 235,786 ACFH

54-3000-101 (9/59) (EF) GEF014
DSI

APP 2B-11

The deliverable shall consist of computer input (GENII) and output files, a description of the assumptions and information used to develop the dose assessment (dose code description, met data, Chi/Q, flow rate and stack height assumptions, etc.), and the signed HDOP review forms.

Radionuclides to be emitted by the HWVP Stacks

H-3,	C-14,	Fe-55,	Ni-59,	Co-60,	Ni-63,	Se-79,	Sr-89,
Sr-90,	Y-90,	Y-91,	Nb-93m,	Zr-93,	Zr-95,	Nb-95,	Tc-99,
Ru-103,	Rh-103m,	Ru-105,	Rh-106,	Pd-107,	Ag-110m,	Cd-113m,	In-113m,
Sn-113,	Cd-115m,	Sn-119m,	Sn-121m,	Sn-123,	Sn-126,	Sb-124,	Sb-126,
Sb-126m,	Sb-125,	Te-125m,	Te-127,	Te-127m,	Te-129,	Te-129m,	I-129,
Cs-134,	Cs-135,	Cs-137,	Ba-137m,	Ce-141,	Ce-144,	Pr-144,	Pr-144m,
Pm-147,	Pm-148m,	Sm-151,	Eu-152,	Gd-153,	Eu-154,	Eu-155,	Tb-160,
U-234,	U-235,	U-236,	U-238,	Np-237,	Pu-238,	Pu-239,	Pu-240,
Pu-241,	Pu-242,	Am-241,	Am-242,	Am-243,	Cm-242,	Cm-244	

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ATTACHMENT 2.

Chi/Q Information

Table 1. Distance from 200 E Area to Site Boundary and Associated Chi/Q.

APP 2B-13

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Table 1. Distance from 200 E Area to Site Boundary and Associated Chi/Q Using 61 m Effective Stack. Strike out indicates distance is within Hanford boundary.

GROUND-LEVEL CHI/Q VALUES FOR H-3
CHI/Q TOWARD INDICATED DIRECTION (SEC/CUBIC METER)

Dir	Distance To Site Boundary	Distance (meters)					
		15200	16200	16900	17200	17600	18100
N	24600	1.736E-08	1.619E-08	1.546E-08	1.517E-08	1.488E-08	1.435E-08
NNW	21600	1.419E-08	1.322E-08	1.263E-08	1.239E-08	1.208E-08	1.171E-08
NW	21400	1.627E-08	1.518E-08	1.441E-08	1.416E-08	1.388E-08	1.337E-08
WNW	21400	1.432E-08	1.331E-08	1.267E-08	1.241E-08	1.209E-08	1.170E-08
W	20800	1.454E-08	1.350E-08	1.285E-08	1.259E-08	1.228E-08	1.186E-08
WSW	21200	9.188E-09	8.516E-09	8.097E-09	7.929E-09	7.715E-09	7.462E-09
SW	17600	1.006E-08	9.317E-09	8.857E-09	8.672E-09	8.437E-09	8.159E-09
SSW	16900	1.247E-08	1.153E-08	1.096E-08	1.072E-08	1.043E-08	1.008E-08
S	19500	2.104E-08	1.950E-08	1.855E-08	1.815E-08	1.768E-08	1.710E-08
SSE	19600	2.188E-08	2.023E-08	1.937E-08	1.898E-08	1.849E-08	1.790E-08
SE	24300	2.640E-08	2.388E-08	2.211E-08	2.168E-08	2.082E-08	2.002E-08
ESE	20000	4.101E-08	3.825E-08	3.652E-08	3.582E-08	3.493E-08	3.388E-08
E	16200	4.044E-08	3.780E-08	3.615E-08	3.548E-08	3.463E-08	3.362E-08
ENE	15200	2.315E-08	2.164E-08	2.070E-08	2.032E-08	1.983E-08	1.925E-08
NE	18100	1.635E-08	1.528E-08	1.460E-08	1.433E-08	1.386E-08	1.357E-08
NNE	23700	1.298E-08	1.212E-08	1.156E-08	1.136E-08	1.100E-08	1.076E-08

* Highest Chi/Q value for offsite area.

Dir	Distance To Site Boundary	Distance (meters)					
		19500	19600	20000	20800	21200	21400
N	24600	1.322E-08	1.315E-08	1.265E-08	1.233E-08	1.208E-08	1.195E-08
NNW	21600	1.078E-08	1.072E-08	1.042E-08	1.005E-08	9.842E-09	9.742E-09
NW	21400	1.228E-08	1.221E-08	1.192E-08	1.143E-08	1.119E-08	1.107E-08
WNW	21400	1.072E-08	1.065E-08	1.041E-08	9.752E-09	9.736E-09	9.632E-09
W	20800	1.025E-08	1.020E-08	1.004E-08	1.008E-08	9.852E-09	9.752E-09
WSW	21200	6.813E-09	6.772E-09	6.513E-09	6.215E-09	6.175E-09	6.108E-09
SW	17600	7.443E-09	7.398E-09	7.224E-09	6.898E-09	6.745E-09	6.671E-09
SSW	16900	9.178E-09	9.122E-09	8.904E-09	8.495E-09	8.304E-09	8.211E-09
S	19500	1.561E-08	1.551E-08	1.515E-08	1.447E-08	1.415E-08	1.400E-08
SSE	19600	1.641E-08	1.631E-08	1.594E-08	1.525E-08	1.492E-08	1.477E-08
SE	24300	2.743E-08	2.734E-08	2.572E-08	2.459E-08	2.505E-08	2.479E-08
ESE	20000	3.121E-08	3.104E-08	3.036E-08	2.910E-08	2.850E-08	2.821E-08
E	16200	3.105E-08	3.089E-08	3.024E-08	2.901E-08	2.843E-08	2.815E-08
ENE	15200	1.779E-08	1.769E-08	1.732E-08	1.662E-08	1.629E-08	1.613E-08
NE	18100	1.253E-08	1.246E-08	1.220E-08	1.170E-08	1.146E-08	1.135E-08
NNE	23700	9.822E-09	9.866E-09	9.857E-09	9.761E-09	9.674E-09	9.635E-09

Table 1. (Cont.) Distance from 200 E Area to Site Boundary and Associated Chi/Q Using 61 m Effective Stack. Strike out indicates distance is within Hanford boundary.

GROUND-LEVEL CHI/Q VALUES FOR H-3
CHI/Q TOWARD INDICATED DIRECTION (SEC/CUBIC METER)

Dir	Distance to Site Boundary	Distance (meters)			
		21600	23700	24300	24600
N	24600	1.183E-08	1.079E-08	1.042E-08	1.028E-08
NNW	21600	9.644E-09	8.716E-09	8.481E-09	8.369E-09
NW	21400	1.096E-08	9.883E-09	9.613E-09	9.483E-09
WNW	21400	9.530E-09	8.568E-09	8.327E-09	8.211E-09
W	20800	9.648E-09	8.673E-09	8.428E-09	8.311E-09
WSW	21200	6.041E-09	5.418E-09	5.262E-09	5.187E-09
SW	17600	6.598E-09	5.916E-09	5.745E-09	5.663E-09
SSW	16900	8.120E-09	7.268E-09	7.055E-09	6.952E-09
S	19500	1.385E-08	1.243E-08	1.207E-08	1.190E-08
SSE	19600	1.461E-08	1.316E-08	1.279E-08	1.261E-08
SE	24300	2.454E-08	2.23E-08	2.153E-08	2.124E-08
ESE	20000	2.792E-08	2.524E-08	2.457E-08	2.424E-08
E	16200	2.788E-08	2.528E-08	2.463E-08	2.431E-08
ENE	15200	1.597E-08	1.449E-08	1.411E-08	1.393E-08
NE	18100	1.124E-08	1.038E-08	9.917E-09	9.789E-09
NNE	23700	8.895E-09	8.056E-09	7.843E-09	7.741E-09

ATTACHMENT 3.

Tables of Dose Analysis results

Table 2. GENII Dose Conversion Factors

Table 3. CAP88-PC Dose Conversion Factors

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Table 2. GENII Dose Conversion Factors for Single Ci/yr Chronic Releases from the Hanford Waste Vitrification Project 200 E Area using 5 yr Meteorological Data. Location of MI: 16000 m East. Values in parentheses indicate the percentage dose from the parent in long-lived decay chain.

	61 m effective stack	59 m stack Buoyant plume rise	67 m stack Buoyant plume rise	59 m stack Momentum plume rise	67 m stack Momentum plume rise
Nuclide	(rem/Ci)	(rem/Ci)	(rem/Ci)	(rem/Ci)	(rem/Ci)
H-3	1.0E-08	1.2E-09	1.7E-09	3.6E-09	4.2E-09
C-14	2.2E-06	2.5E-07	3.5E-07	7.5E-07	8.7E-07
Fe-55	9.5E-08	1.1E-08	1.5E-08	3.3E-08	3.8E-08
Co-60	4.7E-06	5.2E-07	7.3E-07	1.6E-06	1.9E-06
NI-59	2.6E-08	2.9E-09	4.1E-09	9.0E-09	1.0E-08
NI-63	6.9E-08	7.8E-09	1.1E-08	2.4E-08	2.8E-08
Se-79	3.4E-05	3.8E-06	5.4E-06	1.2E-05	1.3E-05
Sr-89	5.9E-07	6.6E-08	9.3E-08	2.0E-07	2.3E-07
Sr-90 (94)	1.8E-05	2.0E-06	2.9E-06	6.2E-06	7.2E-06
Y-90	1.4E-07	1.5E-08	2.2E-08	4.8E-08	5.6E-08
Y-91	9.6E-07	1.1E-07	1.5E-07	3.3E-07	3.8E-07
Zr-93	1.0E-06	1.1E-07	1.5E-07	3.5E-07	4.0E-07
Nb-93M	3.6E-07	4.0E-08	5.6E-08	1.2E-07	1.4E-07
Zr-95 (75)	5.7E-07	6.4E-08	9.0E-08	2.0E-07	2.3E-07
Nb-95	2.2E-07	2.5E-08	3.4E-08	7.3E-08	8.6E-08
Tc-99	1.8E-06	2.0E-07	2.8E-07	6.0E-07	7.2E-07
Ru-103 (100)	2.6E-07	2.9E-08	4.1E-08	9.1E-08	1.1E-07
Rh-103M	3.1E-11	3.4E-12	4.8E-12	1.0E-11	1.2E-11
Ru-106	7.1E-06	7.8E-07	1.1E-06	2.4E-06	2.8E-06
Pd-107	1.6E-07	1.7E-08	2.5E-08	5.5E-08	6.3E-08
Aq-110M	1.0E-05	1.2E-06	1.6E-06	3.6E-06	4.1E-06
Cd-113M	3.4E-05	3.8E-06	5.4E-06	1.2E-05	1.4E-05

(Cont.)

Table 2. GENII Dose Conversion Factors for Single Ci/yr Chronic Releases from the Hanford Waste Vitrification Project 200 E Area using 5 yr Meteorological Data. Location of MI: 16000 m East. Values in parentheses indicate the percentage dose from the parent in long-lived decay chain.

	61 m effective stack	59 m stack Buoyant plume rise	67 m stack Buoyant plume rise	59 m stack Momentum plume rise	67 m stack Momentum plume rise
Nuclide	(rem/Ci)	(rem/Ci)	(rem/Ci)	(rem/Ci)	(rem/Ci)
Cd-115M	1.6E-06	1.8E-07	2.5E-07	5.6E-07	6.5E-07
Sn-113 (86)	4.1E-07	4.7E-08	6.6E-08	1.4E-07	1.6E-07
In-113M	1.7E-09	1.9E-10	2.7E-10	5.7E-10	6.9E-10
Sn-119M	1.9E-07	2.2E-08	3.1E-08	6.7E-08	7.8E-08
Sn-121M (79)	3.7E-07	4.1E-08	5.7E-08	1.3E-07	1.5E-07
Sn-123	1.0E-05	1.2E-07	1.6E-07	3.5E-07	4.1E-07
Sb-125 (86)	6.3E-07	7.1E-08	9.9E-08	2.2E-07	2.6E-07
Te-125M	3.5E-07	4.0E-08	5.5E-08	1.2E-07	1.5E-07
Sn-126 (74)	4.3E-06	4.8E-07	6.7E-07	1.5E-06	1.7E-06
Sb-126M (97)	2.0E-09	2.3E-10	3.1E-10	7.0E-10	8.2E-10
Sb-126	4.7E-07	5.3E-08	7.4E-08	1.6E-07	1.9E-07
Sb-124	1.0E-06	1.2E-07	1.6E-07	3.5E-07	4.1E-07
Te-127M (93)	1.1E-05	1.3E-07	1.9E-07	4.0E-07	4.6E-07
Te-127	3.4E-09	4.1E-10	5.5E-10	1.2E-09	1.4E-09
Te-129M (100)	8.1E-07	9.1E-08	1.3E-07	2.8E-07	3.2E-07
Te-129 (100)	8.2E-10	9.3E-11	1.3E-10	2.9E-10	3.3E-10
I-129	4.4E-04	5.0E-05	6.9E-05	1.5E-04	1.7E-04
Cs-134	1.6E-05	1.8E-06	2.5E-06	5.4E-06	6.3E-06

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(Cont.)

Table 2. GENII Dose Conversion Factors for Single Ci/yr Chronic Releases from the Hanford Waste Vitrification Project 200 E Area using 5 yr Meteorological Data. Location of MI: 16000 m East. Values in parentheses indicate the percentage dose from the parent in long-lived decay chain.

	61 m effective stack	59 m stack Buoyant plume rise	67 m stack Buoyant plume rise	59 m stack Momentum plume rise	67 m stack Momentum plume rise
Nuclide	(rem/Ci)	(rem/Ci)	(rem/Ci)	(rem/Ci)	(rem/Ci)
Cs-135	1.6E-06	1.9E-07	2.6E-07	5.7E-07	6.6E-07
Cs-137	1.2E-05	1.3E-06	1.8E-06	4.0E-06	4.7E-06
Ce-141	2.0E-07	2.3E-08	3.2E-08	7.1E-08	8.2E-08
Ce-144 (100)	5.4E-06	6.0E-07	8.4E-07	1.9E-06	2.2E-06
Pr-144M (2)	6.7E-11	7.6E-12	1.1E-11	2.4E-11	2.7E-11
Pr-144	9.5E-11	1.1E-11	1.5E-11	3.3E-11	3.9E-11
Pm-147	5.1E-07	5.6E-08	7.9E-08	1.8E-07	2.0E-07
Pm-148M (98)	7.8E-07	8.7E-08	1.2E-07	2.7E-07	3.1E-07
Sm-151	3.6E-07	4.0E-08	5.6E-08	1.2E-07	1.4E-07
Eu-152	3.4E-06	3.7E-07	5.2E-07	1.2E-06	1.4E-06
Eu-154	4.3E-06	4.8E-07	6.8E-07	1.5E-06	1.7E-06
Eu-155	5.8E-07	6.4E-08	9.0E-08	2.0E-07	2.3E-07
Gd-153	3.4E-07	3.8E-08	5.3E-08	1.2E-07	1.4E-07
Tb-160	7.6E-07	8.5E-08	1.2E-07	2.6E-07	3.1E-07
U-234	1.5E-03	1.6E-04	2.3E-04	5.1E-04	5.8E-04
U-236	1.4E-03	1.5E-04	2.1E-04	4.8E-04	5.6E-04
U-235	1.4E-03	1.5E-04	2.1E-04	4.7E-04	5.4E-04
Np-237	7.5E-03	8.2E-04	1.2E-03	2.6E-03	3.0E-03
U-238	1.3E-03	1.4E-04	2.0E-04	4.5E-04	5.2E-04
Am-242 (93)	6.1E-07	6.7E-08	9.5E-08	2.0E-07	2.3E-07

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(Cont.)

Table 2. GENII Dose Conversion Factors for Single Ci/yr Chronic Releases from the Hanford Waste Vitrification Project 200 E Area using 5 yr Meteorological Data. Location of HI: 16000 m East. Values in parentheses indicate the percentage dose from the parent in long-lived decay chain.

	61 m effective stack	59 m stack Buoyant plume rise	67 m stack Buoyant plume rise	59 m stack Momentum plume rise	67 m stack Momentum plume rise
Nuclide	(rem/Ci)	(rem/Ci)	(rem/Ci)	(rem/Ci)	(rem/Ci)
Cm-242 (100)	1.9E-04	2.1E-05	2.9E-05	6.5E-05	7.5E-05
Pu-242 (100)	3.2E-03	3.5E-04	5.0E-04	1.1E-03	1.3E-03
Pu-238	3.2E-03	3.4E-04	4.9E-04	1.1E-03	1.3E-03
Cm-244	2.9E-03	3.2E-04	4.5E-04	1.0E-03	1.2E-03
Pu-240	3.3E-03	3.6E-04	5.2E-04	1.2E-03	1.3E-03
Pu-241	5.4E-05	5.9E-06	8.4E-06	1.9E-05	2.2E-05
Am-241	5.1E-03	5.6E-04	7.9E-04	1.8E-03	2.0E-03
Am-243	5.1E-03	5.6E-04	7.9E-04	1.8E-03	2.0E-03
Pu-239	3.3E-03	3.6E-04	5.2E-04	1.2E-03	1.3E-03

Note: Rh-106 and Ba-137m are short-lived decay products and are implicitly included in the dose factor of the parent radionuclide

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Table 3. CAP88-PC Dose Conversion Factors for unit Ci/yr Releases from the Hanford Waste Vitrification Project 200 E Area Using 5 Yr, 10 m Meteorological Data (Location of MI: 16000 m East)

	61 m effective stack	59 m stack, Buoyant plume rise	67 m stack, Buoyant plume rise	59 m stack, Momentum plume rise	67 m stack, Momentum plume rise
Nuclide	(mrem/Ci)	(mrem/Ci)	(mrem/Ci)	(mrem/Ci)	(mrem/Ci)
H-3	1.2E-05	5.3E-06	5.5E-06	7.9E-06	8.0E-06
C-14	6.6E-04	2.9E-04	3.1E-04	4.4E-04	4.4E-04
Fe-55	1.8E-04	9.6E-05	9.9E-05	1.3E-04	1.3E-04
Co-60	8.2E-02	4.4E-02	4.6E-02	6.0E-02	6.0E-02
Ni-59	1.5E-04	8.2E-05	8.5E-05	1.1E-04	1.1E-04
Ni-63	1.7E-04	8.8E-05	9.1E-05	1.2E-04	1.2E-04
Se-79 *	0.0E+00	0.0E+00	0.0E+00	0.0E+00	0.0E+00
Sr-89	8.0E-04	4.3E-04	4.4E-04	5.8E-04	5.8E-04
Sr-90 **	5.9E-02	3.2E-02	3.3E-02	4.3E-02	4.3E-02
Y-90	1.2E-04	5.4E-05	5.6E-05	7.9E-05	7.9E-05
Y-91	1.3E-03	6.6E-04	6.8E-04	9.2E-04	9.2E-04
Nb-93m	1.8E-03	9.3E-04	9.6E-04	1.3E-03	1.3E-03
Zr-93	7.3E-04	3.5E-04	3.7E-04	5.1E-04	5.1E-04
Zr-95 **	1.9E-03	1.0E-03	1.0E-03	1.4E-03	1.4E-03
Nb-95	1.9E-03	1.0E-03	1.1E-03	1.4E-03	1.4E-03
Tc-99	1.2E-02	6.3E-03	6.5E-03	8.5E-03	8.5E-03
Ru-103	6.9E-04	3.6E-04	3.7E-04	4.9E-04	5.0E-04
Ru-106	8.7E-03	4.3E-03	4.4E-03	6.0E-03	6.1E-03
Rh-103m	3.2E-08	1.6E-08	1.6E-08	2.3E-08	2.3E-08
Rh-106	7.6E-36	4.4E-36	4.5E-36	6.0E-36	6.0E-36
Pd-107	2.1E-04	1.0E-04	1.1E-04	1.4E-04	1.5E-04
Ag-110m	1.7E-02	9.0E-03	9.3E-03	1.2E-02	1.2E-02
Cd-113m *	0.0E+00	0.0E+00	0.0E+00	0.0E+00	0.0E+00
Cd-115m	1.7E-03	8.9E-04	9.2E-04	1.2E-03	1.2E-03
In-113m	1.4E-06	6.9E-07	7.2E-07	9.9E-07	1.0E-06
Sn-113 **	2.0E-03	1.1E-03	1.1E-03	1.4E-03	1.4E-03

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(Cont.)

Table 3. CAP88-PC Dose Conversion Factors for unit Ci/yr Releases from the Hanford Waste Vitrification Project 200 E Area Using 5 Yr, 10 m Meteorological Data (Location of MI: 16000 m East)

	61 m effective stack	59 m stack, Buoyant plume rise	67 m stack, Buoyant plume rise	59 m stack, Momentum plume rise	67 m stack, Momentum plume rise
Nuclide	(mrem/Ci)	(mrem/Ci)	(mrem/Ci)	(mrem/Ci)	(mrem/Ci)
Sn-123	1.6E-05	8.6E-06	8.9E-06	1.2E-05	1.2E-05
Sn-126	3.0E-02	1.6E-02	1.7E-02	2.2E-02	2.2E-02
Sb-124	3.1E-03	1.6E-03	1.7E-03	2.2E-03	2.2E-03
Sb-125 **	9.6E-03	5.2E-03	5.4E-03	7.0E-03	7.0E-03
Sb-126	1.1E-03	5.8E-04	6.0E-04	7.9E-04	7.9E-04
Sb-126m	7.3E-07	4.0E-07	4.2E-07	5.6E-07	5.6E-07
Te-125m	5.4E-04	2.9E-04	3.0E-04	3.9E-04	3.9E-04
Te-127	4.5E-06	2.1E-06	2.2E-06	3.1E-06	3.1E-06
Te-127m **	1.7E-03	9.0E-04	9.2E-04	1.2E-03	1.2E-03
Te-129	7.9E-07	3.8E-07	4.0E-07	5.5E-07	5.6E-07
Te-129m	1.2E-03	6.1E-04	6.3E-04	8.3E-04	8.4E-04
I-129	6.7E-01	5.8E-01	5.9E-01	6.4E-01	6.5E-01
Cs-134	4.5E-02	2.4E-02	2.5E-02	3.3E-02	3.3E-02
Cs-135	3.3E-03	1.8E-03	1.8E-03	2.4E-03	2.4E-03
Cs-137 ***	8.5E-02	4.6E-02	4.8E-02	6.2E-02	6.2E-02
Ba-137m	4.0E-12	2.3E-12	2.4E-12	3.1E-12	3.1E-12
Ce-141	3.3E-04	1.7E-04	1.8E-04	2.4E-04	2.4E-04
Ce-144	6.6E-03	3.3E-03	3.4E-03	4.6E-03	4.7E-03
Pr-144	5.6E-08	3.1E-08	3.2E-08	4.3E-08	4.3E-08
Pr-144m **	5.3E-08	3.1E-08	3.2E-08	4.2E-08	4.2E-08
Pm-147	6.1E-04	2.9E-04	3.1E-04	4.2E-04	4.2E-04
Pm-148m **	3.0E-03	1.6E-03	1.6E-03	2.1E-03	2.2E-03
Sm-151	4.2E-04	2.0E-04	2.1E-04	2.9E-04	2.9E-04
Eu-152	7.9E-02	4.2E-02	4.4E-02	5.7E-02	5.7E-02
Eu-154	6.3E-02	3.4E-02	3.5E-02	4.6E-02	4.6E-02

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(Cont.)

Table 3. CAPBB-PC Dose Conversion Factors for unit Ci/yr Releases from the Hanford Waste Vitrification Project 200 E Area Using 5 Yr, 10 m Meteorological Data (Location of MI: 16000 m East)

	61 m effective stack	59 m stack, Buoyant plume rise	67 m stack, Buoyant plume rise	59 m stack, Momentum plume rise	67 m stack, Momentum plume rise
Nuclide	(mrem/Ci)	(mrem/Ci)	(mrem/Ci)	(mrem/Ci)	(mrem/Ci)
Eu-155	2.8E-03	1.5E-03	1.5E-03	2.0E-03	2.0E-03
Tb-160	2.4E-03	1.3E-03	1.3E-03	1.7E-03	1.7E-03
U-234	1.7E+00	7.9E-01	8.2E-01	1.2E+00	1.2E+00
U-235	1.6E+00	7.5E-01	7.8E-01	1.1E+00	1.1E+00
U-236	1.6E+00	7.5E-01	7.8E-01	1.1E+00	1.1E+00
U-238	1.5E+00	7.1E-01	7.3E-01	1.0E+00	1.0E+00
Np-237	6.3E+00	3.0E+00	3.1E+00	4.3E+00	4.3E+00
Pu-238	4.1E+00	2.0E+00	2.0E+00	2.8E+00	2.9E+00
Pu-239	4.5E+00	2.1E+00	2.2E+00	3.1E+00	3.1E+00
Pu-240	4.5E+00	2.1E+00	2.2E+00	3.1E+00	3.1E+00
Pu-241	7.0E-02	3.3E-02	3.5E-02	4.8E-02	4.8E-02
Pu-242	4.2E+00	2.0E+00	2.1E+00	2.9E+00	2.9E+00
Am-241	6.9E+00	3.2E+00	3.4E+00	4.7E+00	4.7E+00
Am-242 **	7.1E-04	3.3E-04	3.4E-04	4.8E-04	4.8E-04
Am-243	6.9E+00	3.2E+00	3.4E+00	4.7E+00	4.7E+00
Cm-242	2.2E-01	1.0E-01	1.1E-01	1.5E-01	1.5E-01
Cm-244	3.6E+00	1.7E+00	1.8E+00	2.5E+00	2.5E+00
-	CAPBB-PC Does not include dose factors for Se-79 or Cd-113m				
**	Dose includes the ingrowth of progeny calculated by dividing CAPBB-PC results by fraction of dose from parent derived by GENII runs.				
***	Dose includes ingrowth of Ba-137m added to Cs-137 dose. Fraction of dose from Cs-137 is 23 percent.				

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ATTACHMENT 4.

Application Record Log

APP 2B-27

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APPLICATION RECORD LOG

1) Project title and number: Hanford Waste Vitrification Program ED2505

2) Application Record Log Number	3) Date and Time of Run	4) Software Name (title) and Version	5) computer type operating system compilers/libraries	6) Comments	7) Data Input Identifier
Filename (a)	see below	CAPDDPC Version 1.0	IDM PS/2, DOS 3.30	see below	see below

Directory of F:\HWVP\CAPDDPC

59D10M3 SUM 11170 06-04-92 1:28p
 59D10M2 SUM 11319 06-04-92 12:00p
 59H10M1 SUM 11040 06-04-92 1:30p
 59H10M2 SUM 11431 06-04-92 1:36p
 59H10M3 SUM 11394 06-04-92 2:53p
 59D10M1 SUM 11040 06-04-92 11:59a
 61E10M2 SUM 11504 06-04-92 1:40p
 61E10M1 SUM 11040 06-04-92 1:38p
 61E10M3 SUM 11243 06-04-92 1:42p
 67D10M1 SUM 11040 06-04-92 1:44p
 67D10M2 SUM 11431 06-04-92 1:53p
 67D10M3 SUM 11170 06-04-92 1:45p
 67H10M1 SUM 11040 06-04-92 1:46p
 67H10M2 SUM 11431 06-04-92 1:48p
 67H10M3 SUM 11170 06-04-92 2:54p

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2) Application Record Log Number	3) Date and Time of Run	4) Software Name (title) and Version	5) computer type operating system compilers/libraries	6) Comments	7) Data Input Identifier
Filename (a)	see below	GENII version 1.405	IDM PS/2, DOS 3.30	see below	see below

DOE/RL-52-41, Rev. 1
09/25/92

TITLE	INR	ING	EXI	COE	ORGAN D	UNIT	ORG	PTH	MUC	RUN DATE	TIME	SIP	ENVIRONMENTAL	EXP PATH	TIME
File				(Intri)								(near/ac/pop)			(linrel/com)
NP61E PARENT MUC:	2.0E-02	9.8E-04	6.4E-06	2.1E-02	3.1E-01	rem	Bon	Irsh	NP237	04/14/92	14:40	fff			1 150
ND161E DECAT MUC:	1.3E-02	6.8E-04	1.6E-07	1.5E-02	1.9E-01	rem	Bon	Irsh	AH241	04/14/92	14:42	fff			1 150
ND261E DECAT MUC:	3.2E-03	3.0E-06	2.2E-09	3.2E-03	3.1E-02	rem	Bon	Irsh	PU242	04/14/92	14:43	fff			1 150
ND361E DECAT MUC:	1.8E-04	7.1E-06	5.6E-12	1.9E-04	2.1E-03	rem	Bon	Irsh	CH242	04/14/92	14:45	fff			1 150
NP59H PARENT MUC1:	7.0E-03	3.4E-04	2.2E-06	7.3E-03	1.1E-01	rem	Bon	Irsh	NP237	04/16/92	16:40	fff			1 150
ND159H DECAT 1 MUC:	5.1E-03	2.3E-04	5.6E-06	5.3E-03	6.6E-02	rem	Bon	Irsh	AH241	04/16/92	16:41	fff			1 150
ND29H DECAT 1 MUC1:	1.1E-03	1.0E-06	7.7E-10	1.1E-03	1.1E-02	rem	Bon	Irsh	PU242	04/16/92	16:43	fff			1 150
ND359H DECAT 1 MUC:	6.3E-03	2.5E-06	2.0E-12	6.5E-03	7.2E-04	rem	Bon	Irsh	CH242	04/16/92	16:44	fff			1 150
NP59H PARENT MUC1:	2.2E-03	1.1E-04	7.4E-07	2.3E-03	3.4E-02	rem	Bon	Irsh	NP237	04/16/92	16:52	fff			1 150
ND159H DECAT MUC1:	1.6E-03	7.7E-05	1.0E-08	1.7E-03	2.1E-02	rem	Bon	Irsh	AH241	04/16/92	16:53	fff			1 150
ND259H DECAT MUC1:	3.5E-04	3.4E-07	2.6E-10	3.5E-04	3.4E-03	rem	Bon	Irsh	PU242	04/16/92	16:55	fff			1 150
ND359H DECAT MUC1:	2.0E-03	8.1E-07	6.7E-13	2.1E-03	2.3E-04	rem	Bon	Irsh	CH242	04/16/92	16:56	fff			1 150
NP67H PARENT MUC1:	8.1E-03	4.0E-04	2.6E-06	8.5E-03	1.2E-01	rem	Bon	Irsh	NP237	04/16/92	17:04	fff			1 150
ND167H DECAT 1 MUC:	5.9E-03	2.7E-04	6.5E-06	6.2E-03	7.7E-02	rem	Bon	Irsh	AH241	04/16/92	17:05	fff			1 150
ND267H DECAT 1 MUC:	1.3E-03	1.2E-06	9.6E-10	1.3E-03	1.2E-02	rem	Bon	Irsh	PU242	04/16/92	17:07	fff			1 150
ND367H DECAT 1 MUC:	7.3E-05	2.9E-06	2.3E-12	7.5E-05	8.3E-04	rem	Bon	Irsh	CH242	04/16/92	17:08	fff			1 150
NP67H PARENT MUC1:	3.1E-03	1.6E-04	1.0E-06	3.3E-03	4.8E-02	rem	Bon	Irsh	NP237	04/16/92	17:16	fff			1 150
ND167H DECAT 1 MUC:	2.3E-03	1.1E-04	2.6E-08	2.4E-03	3.0E-02	rem	Bon	Irsh	AH241	04/16/92	17:18	fff			1 150
ND267H DECAT 1 MUC:	5.0E-04	4.7E-07	3.0E-10	5.0E-04	4.8E-03	rem	Bon	Irsh	PU242	04/16/92	17:19	fff			1 150
ND367H DECAT 1 MUC:	2.0E-03	1.1E-06	9.0E-13	2.9E-03	3.2E-04	rem	Bon	Irsh	CH242	04/16/92	17:20	fff			1 150

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(a) The filename is included in the title. A unique filename is given for each run.

(b) Prepared by:

[Handwritten Signature]
Signature

6/11/92
Date

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09/25/92

APPENDIX B

EXCERPTS FROM TANK WASTE TECHNICAL OPTIONS REPORT,
WHC-EP-0616, REV. 0, 1993
(RETRIEVAL)

6.2	SELECTION OF RETRIEVAL TECHNOLOGY OPTIONS
6.3	WASTE RETRIEVAL OPTIONS
F3.2	TECHNOLOGY SELECTION
F3.3	RETRIEVAL AND TRANSFER FUNCTION ELEMENTS
F10.0	REFERENCES

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6.2 SELECTION OF RETRIEVAL TECHNOLOGY OPTIONS

The following describes the process for selection of the retrieval technology options evaluated in this chapter. The selection followed an extensive review of technologies in use and under development in the mining, environmental remediation technology, and demolition industries, and previously published studies, reports, and workshops. Other technology options can be evaluated as they become available. Figure 6-1 identifies the technology options and highlights those that were evaluated in this report. Appendix F provides a more detailed discussion of retrieval technologies that were not evaluated in this chapter.

Because the retrieval function is integrated with the tank closure function, the selection of options were chosen to satisfy a range of closure alternatives from treating the empty tank in place to complete tank removal. Thus the initial logic pathway divided options along either multi- or single- purpose paths where 'multi-purpose' considers options with the capabilities for both waste retrieval and tank and soil removal while 'single purpose' options address waste retrieval only and a limited interface with closure.

With respect to the multi-purpose options, two representative options were considered. 'Open tank mining' describes an array of options which rely on mobile surface or subsurface based equipment to penetrate the tank, retrieve the waste, then remove the tank, etc. The 'large arm' refers to an option which relies on equipment, single or multiple arms, suspended from an overhead structure to perform the retrieval/removal tasks. Both options require a substantial confinement facility for operations. The developed technology for mining, excavation and demolition is extensive, but it was concluded that its adaptation to the radioactive environment would require considerable redesign and development resulting in an exceedingly complex and potentially impractical systems. The 'large arm' supported from an overhead trolley fitted with changeable end effectors appeared to be the most adaptable option and was selected for the study.

The 'single purpose' options range from those technically well developed such as dredging and sluicing to the highly theoretical such as 'waste vaporization.' Those that required basic research and development without significant payback potential, such as 'waste vaporization' and 'thermal shock' were disregarded. Technologies which were well developed but found too limited or complex to apply to general retrieval use were also disregarded. Hydraulic mining and dredging fall into this category. Each could potentially be used for a specific waste form or tank environment but not suitable for general use. Another category of options which includes robotic, tunnel, and tethered mining were disregarded because of the complexity in adapting these technologies to the radioactive waste environment.

The 'single purpose' options carried in the report include the long-reach arm, sluicing and mixers (limited to DSTs only). Sluicing and mixer technologies have been previously used and sufficiently demonstrated for all forms of tank waste. Robotic, long-reach arm technologies, though not used on the scale or in the environment, called for here, appears to carry the most potential in providing the flexibility and adaptability in dealing with the

various waste forms and particularly the tank environment, i.e. in-tank hardware, access through the tank dome.

Of particular concern with 'sluicers' and its introduction of free liquid into a tank is the potential for leaks. From a technology standpoint, only subsurface barriers were carried as a technology enhancement to the sluicing option. Other options which achieved 'tank sealing' were disregarded because of a lack of technical basis. Micro silica colloid addition and permeation grouting of the tank shell were included in these options.

The options that follow the logic pathway from the 'long-reach arm' include the array of the major end effector technologies noted in the report. None are specifically evaluated in the report because it is expected that in all cases some development will be necessary in adaptation to the arm, tank waste form and tank environment. Those technologies noted appear to have the broadest application to the retrieval task.

The options which follow the logic pathways from 'sluicers' and 'mixers' primarily describe technologies which are used to supplement or implement the primary option selected. They reflect technologies which can be applied in a direct manner with little further development. Some of the technologies noted are not compatible with 'mixers', e.g. water cannon.

6.3 WASTE RETRIEVAL OPTIONS

The retrieval function is comprised of process elements required to perform the combined waste retrieval and transfer tasks. Each element contains several selected technologies expected to result in satisfactory performance. These elements are illustrated in Figure 6-2 and the technologies are described in the following sections. The retrieval options are selectively combined with transfer and confinement options described in Sections 6.4 and 6.5.

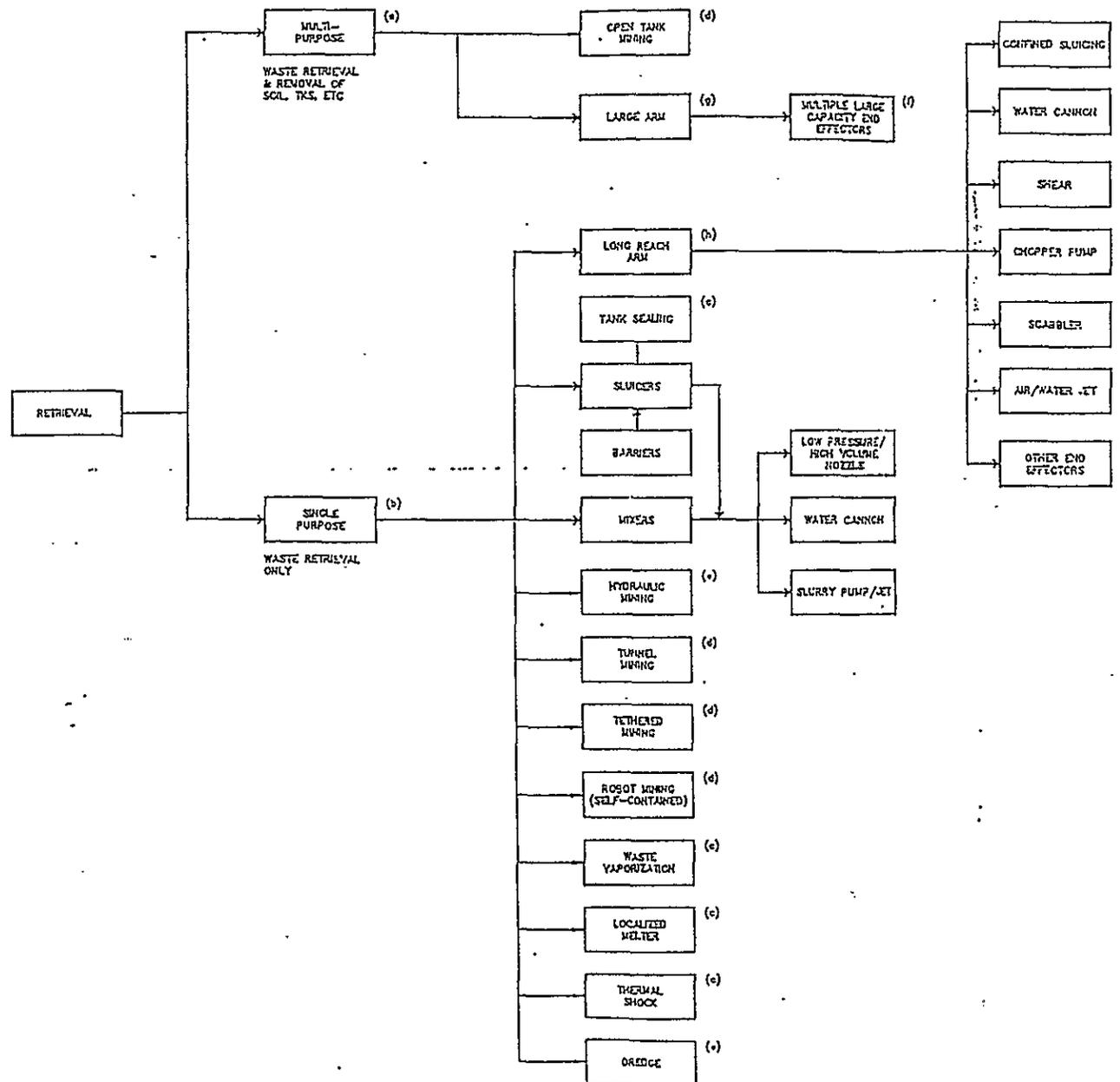
The specific areas where the retrieval function elements vary with respect to the options listed in Figure 6-2 are as follows:

- Tank waste conveyance
- End effectors
- Tank preparation
- Confinement
- Maneuvering and control
- Debris waste removal.

A retrieval option is identified or named by the method used to remove waste from the tank to the surface rather than the type of end effector used to mobilize the waste. Retrieval options with the same name can vary as to layout, method of deployment, end effector, etc., depending on the interfaces dictated by a particular alternative, but functionally they will

RETRIEVAL TECHNOLOGY OPTIONS

Figure 6-1. Retrieval Technology Options.



LEGEND:

OPTION EVALUATED IN CHAPTER 6.

OPTION NOT CONSIDERED IN CHAPTER 6.

NOTES:

- (a) CONFINEMENT TYPICALLY PROVIDED BY FACILITY CONCEPTS WHICH ENCLOSE THE ENTIRE SURFACE AREA ABOVE A TANK.
- (b) CONFINEMENT TYPICALLY PROVIDED BY THE TANK ITSELF AND ENCLOSURES AROUND OPERATING EQUIPMENT LOCATED IN TANK RISERS OR PENETRATIONS.
- (c) BASIC RESEARCH AND DEVELOPMENT REQUIRED BEFORE THESE TECHNOLOGIES CAN BE FURTHER EVALUATED.
- (d) MECHANICAL AND CONTROL COMPLEXITY REQUIRED IN ADAPTING TECHNOLOGIES TO THE RADIOACTIVE WASTE ENVIRONMENT DEFEAT PERCEIVED BENEFITS.
- (e) THESE TECHNOLOGIES ARE DEVELOPED BUT FOUND TOO LIMITED OR TOO COMPLEX TO APPLY FOR GENERAL RETRIEVAL USE; MAY BE SUITABLE FOR LIMITED APPLICATION IN SOME FORM.
- (f) END EFFECTORS USE DEMONSTRATED COMMERCIAL TECHNOLOGIES FOR WASTE INCUBIZATION. MUST INTERFACE WITH HANDLING AND TRANSFER SYSTEMS.
- (g) LARGE CAPACITY, SHORT REACH ARM USED FOR WASTE RETRIEVAL AND TANK SOIL PUMPING, ETC. REMOVAL; CAPABLE OF RELATIVELY HIGH RETRIEVAL PRODUCTION RATES. MULTIPLE END EFFECTORS USED FOR GENERAL TASKS.
- (h) LONG REACH ARM USED FOR WASTE RETRIEVAL ONLY; LIMITED CAPACITY AND CAPABILITY IN HANDLING BY TANK HARDWARE AND OTHER TASKS. MULTIPLE END EFFECTORS USED FOR SPECIFIC TASKS.

Figure 6-2. Retrieval Function Elements.
(sheet 1 of 2)

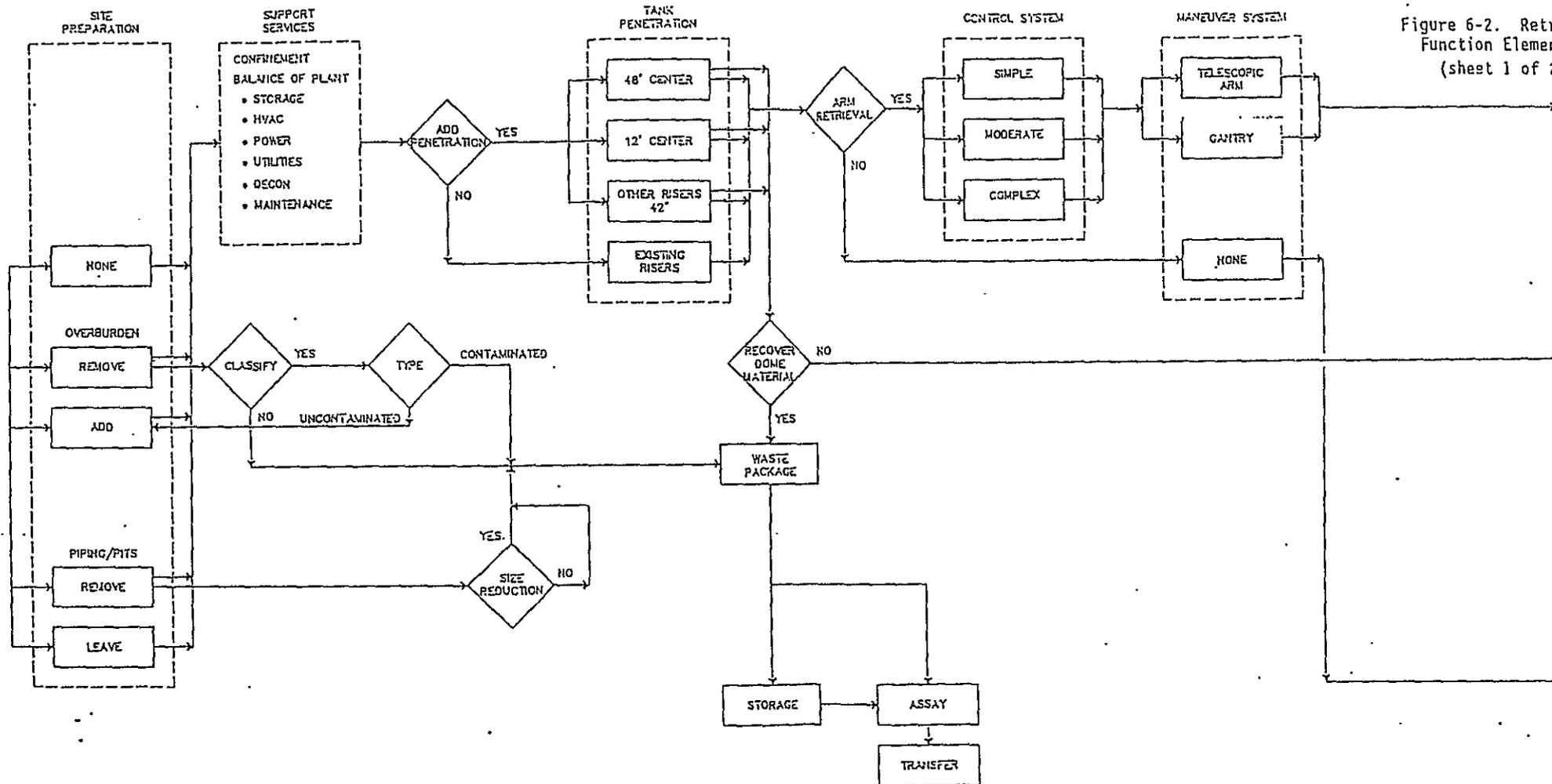
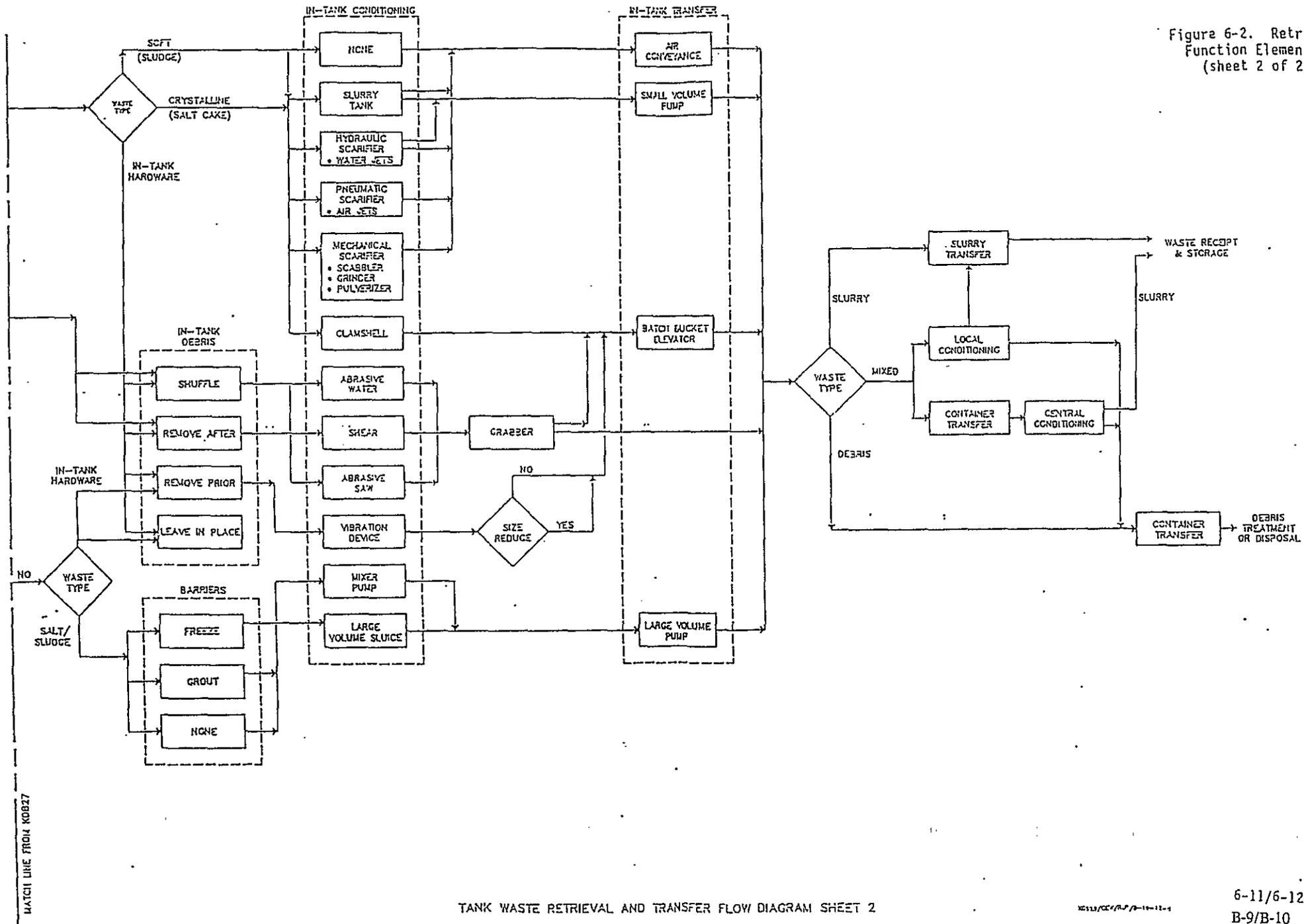


Figure 6-2. Retrieval Function Elements.
(sheet 2 of 2)



perform the same. Due to the nature of DST wastes and the inherent advantages of operating in double-walled tanks, retrieval methods for DSTs are limited to hydraulic options only.

6.3.1 Single-Shell Tank Waste Retrieval Options

The following three retrieval options are assumed capable of retrieving all SST waste forms. These options include maneuvering and waste handling systems to compliment the retrieval methods selected. Detailed descriptions and costs of the options are located in Appendix F.

6.3.1.1 Mechanical Retrieval. The mechanical retrieval system uses a mechanical conveyance, such as a bucket, skip hoist, or conveyor to move waste out of the tank. The mechanical system consists of components as depicted in Figure 6-3.

Mechanical retrieval requires an arm based maneuvering device with end effectors to break up and mobilize tank waste remotely, move debris waste, pick up tank waste, and deposit all waste into a bucket. When the bucket is full it is withdrawn from the tank for load out to the tank waste transfer system. Any debris waste to be removed will use the same conveyance system. Though a continuous conveyor may be used, the waste mobilization process will likely be a multi-step batch process, i.e., digging, rubblizing, pickup, deposit, transfer.

6.3.1.2 Pneumatic Retrieval. Pneumatic retrieval uses an enclosed, high velocity, air stream to suspend the waste and carry it out of the tank. A maneuvering system similar to the one described for mechanical retrieval is used to provide access to the waste.

The air conveyance or pneumatic system (see Figure 6-4) has three key elements: the positive displacement blower, suction hose, and cyclone separator. The blower creates a high velocity air stream in a suction hose. The hose leads to a cyclone separator which removes both solid and liquid particles from the airstream. The waste is drawn into the hose, suspended in the air stream, and transferred to the separator.

Pneumatic systems can transport considerable distances. Some water may be added to the air stream, particularly when transferring heavy sludges, to facilitate material suspension and eliminate plugging problems.

All equipment in the system, except the suction hose and maneuvering arm, is located outside of the tank. This reduces maneuvering system loads and improves reliability. The system moves any material, sludge, salt cake or debris, that can be suspended in the airstream. Air jets, water jets, or mechanical means may be used by end effectors to break up and mobilize the waste for transfer. Air conveyance cannot remove large debris waste. If debris removal is required, an appropriate arm and/or end effectors suited to debris removal must be used with a debris transfer system.

Figure 6-3. Mechanical Retrieval.

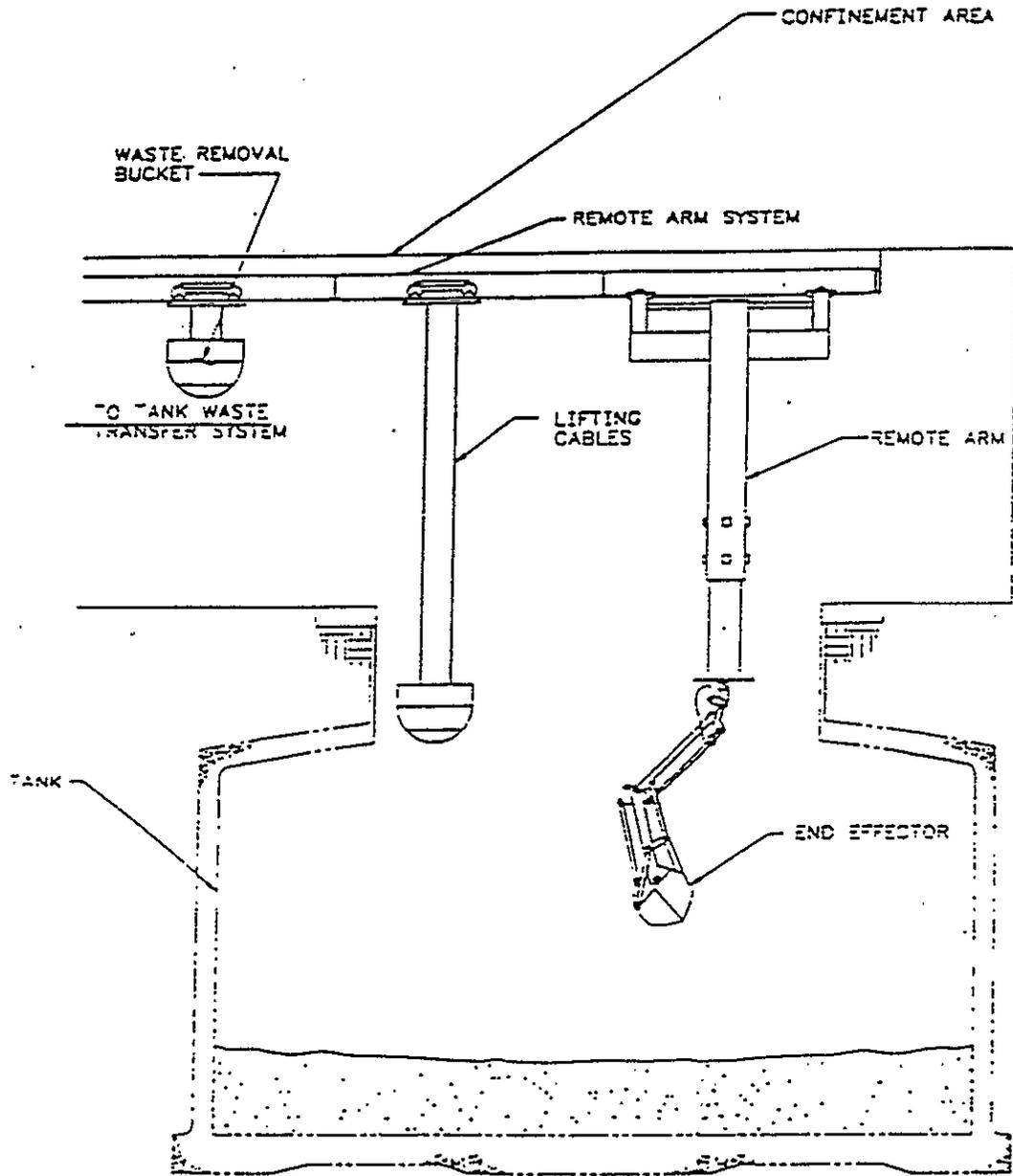
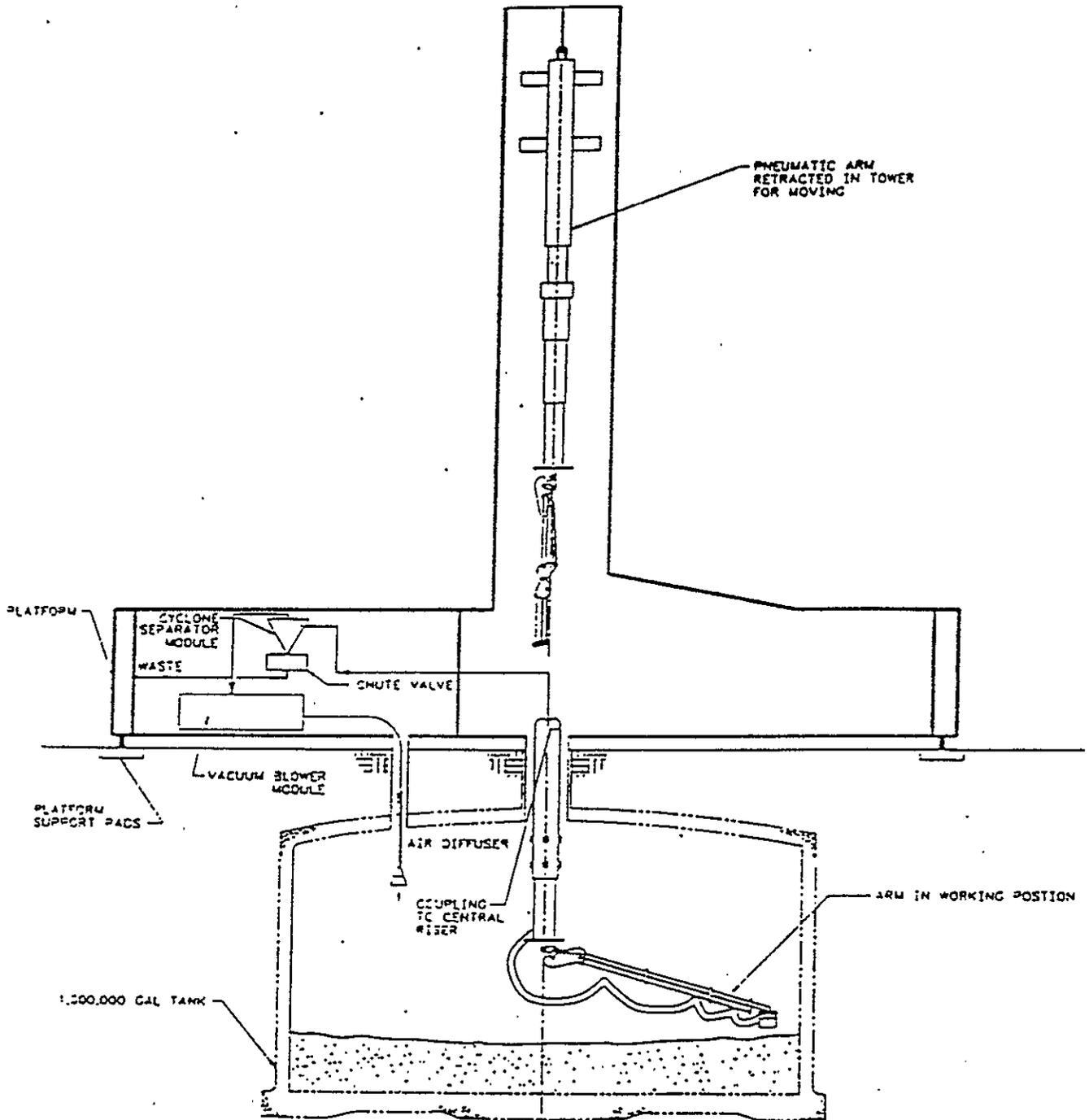


Figure 6-4. Pneumatic Retrieval.



6.3.1.3 Hydraulic Retrieval. A hydraulic retrieval system uses slurry transfer (pumping) to move the tank waste out of the tank. The equipment includes high-pressure, high-volume water jets with associated pumping and supply systems as well as accumulation tanks and recirculation systems. Water jet action dislodges and mobilizes the waste, dissolves or breaks it down, and washes the waste to a slurry pump where it is pumped to the surface and to the accumulation tanks. Here the material is staged for recirculation and eventual transfer to storage. A key goal of hydraulic retrieval is to remove the maximum amount of waste with the minimum amount of free liquid.

Two concepts of hydraulic retrieval are carried in the study. They differ only in how the water jet is maneuvered within the tank. 'Limited sluicing' relies on an arm based system (Figure 6-5) to achieve precise maneuvering of a jet and/or nozzle, while the other, called 'large volume sluicing' or simply 'sluicing' uses individual, riser mounted devices with more limited maneuverability (Figure 6-6). Two types of sluicers are depicted. The first is a traditional sluicer with only vertical and horizontal nozzle rotation. The second type is an enhanced sluicer, which offers both rotation, translation, etc.

The riser mounted system was the method successfully used in the past retrieval campaigns noted in Section 6.1.1. As with pneumatic retrieval, hydraulic retrieval cannot remove large debris waste.

A key issue with hydraulic retrieval is the potential for leaking contaminated liquid to the soil. A summary of the methods for leak mitigation are described in the following paragraphs. Further details on the mitigation methods and the implications of leaks may be found in Appendix F.

Subsurface barriers may be incorporated with hydraulic retrieval. The barriers are placed throughout an entire farm as part of site preparation. The barrier may not prevent contaminants from reaching the groundwater. But it slows migration sufficiently to allow for remediation of the contaminated soil as part of closure. Soil flushing, immobilization, in situ vitrification and soil removal are some of the soil remediation technologies evaluated in Chapter 13.0.

Surface or intrusion barriers may be used to prevent soil recharge and thus greatly slow and diffuse contaminant migration. These barriers would be placed over an entire farm site as part of a closure strategy.

Leakage from tanks may be minimized or eliminated in most tanks by operating with a minimum free liquid depth [approximately .33 m (1 ft)]. Most SST leaks are believed to be higher in the tank wall at past liquid/vapor interfaces.

The prevention or plugging of tank leaks is potentially the most desirable method of leak mitigation. For example, permeation grout placed next to the UGT surfaces would

Figure 6-5. Hydraulic Retrieval--Arm Based.

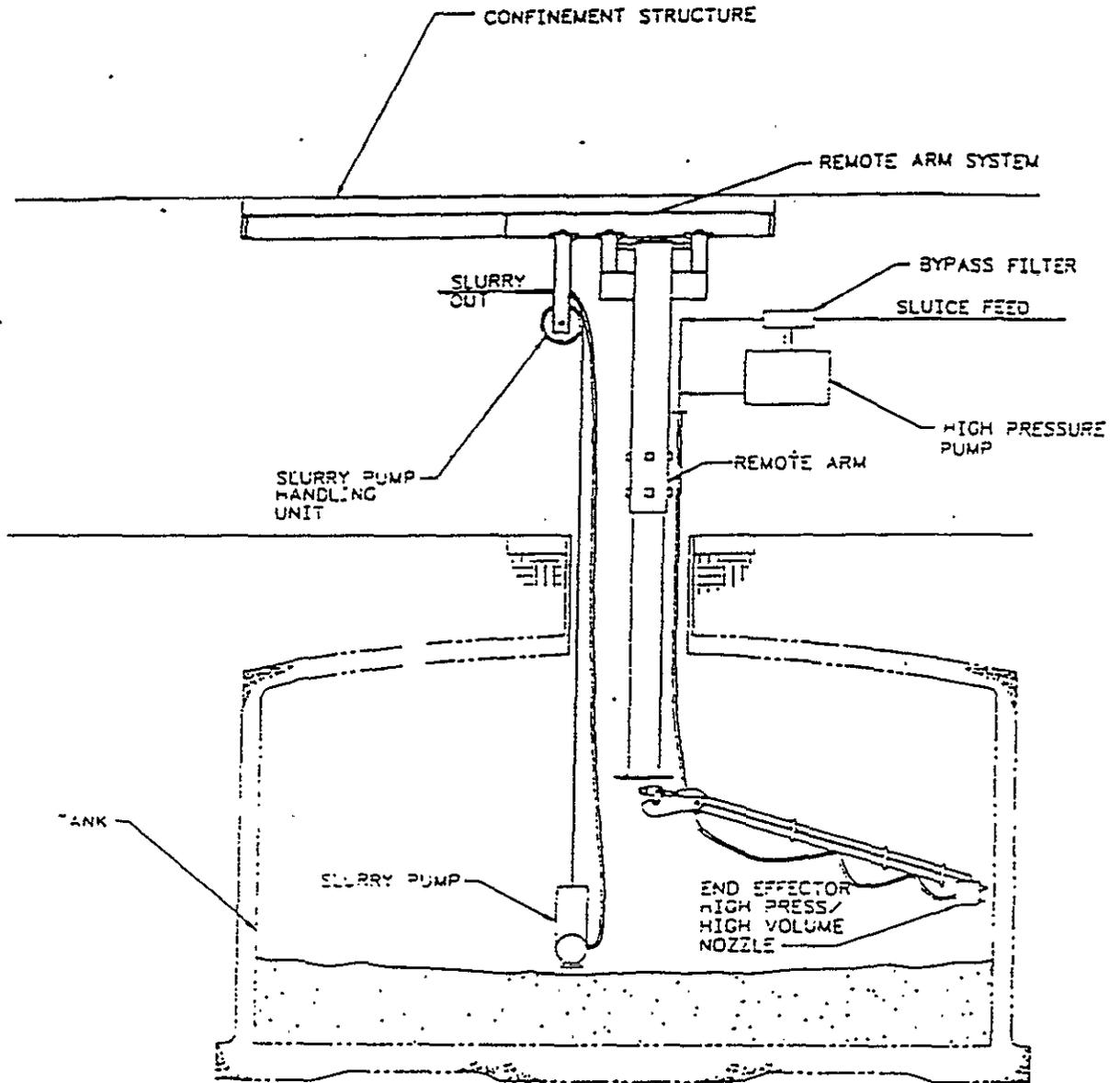
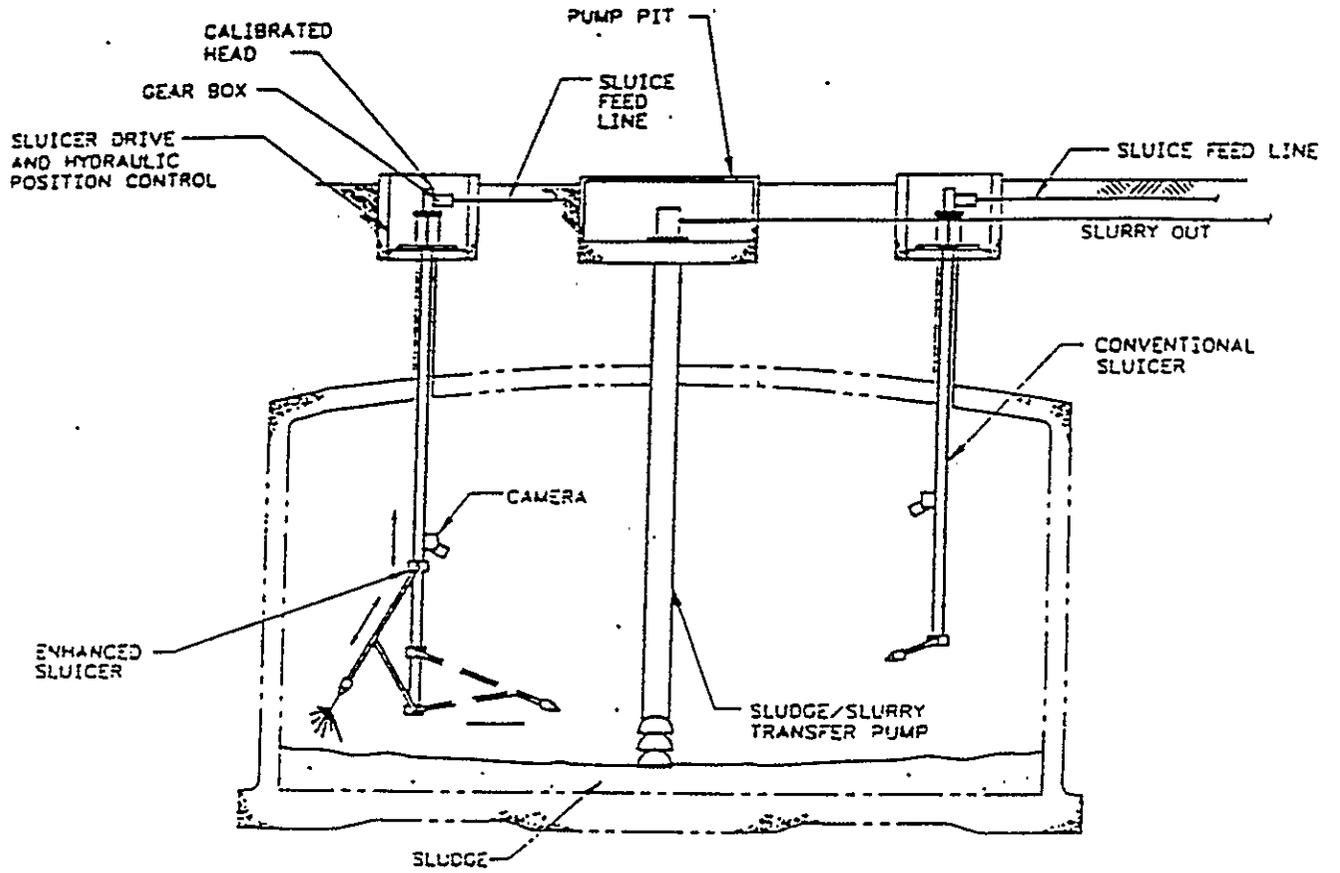


Figure 6-6. Hydraulic Retrieval-Sluicer.



effectively encapsulate or cocoon a tank to prevent leaks. A number of promising technologies exist to accomplish this but, to date, none have been developed sufficiently nor demonstrated.

It is important to note that most mitigation methods rely on an integrated strategy with closure actions for satisfactory results. Any leak remediation whether instituted for existing or new leaks (as the result of sluicing) must be implemented as part of an approved closure plan. More than 2.85×10^6 L (753,000 gal) have already leaked or spilled to the soil.

6.3.2 Double-Shell Tank Waste Retrieval Options

More than 80 percent of the DST inventory is liquid with little salt cake and sludges. This combination of waste forms is particularly suited to the hydraulic retrieval option previously described in Section 6.3.1.3. The DST non liquid wastes can be mobilized through the action of liquid jets and transferred as a slurry. The double-walled tank construction is particularly suited to hydraulic retrieval because it eliminates the potential of leaks.

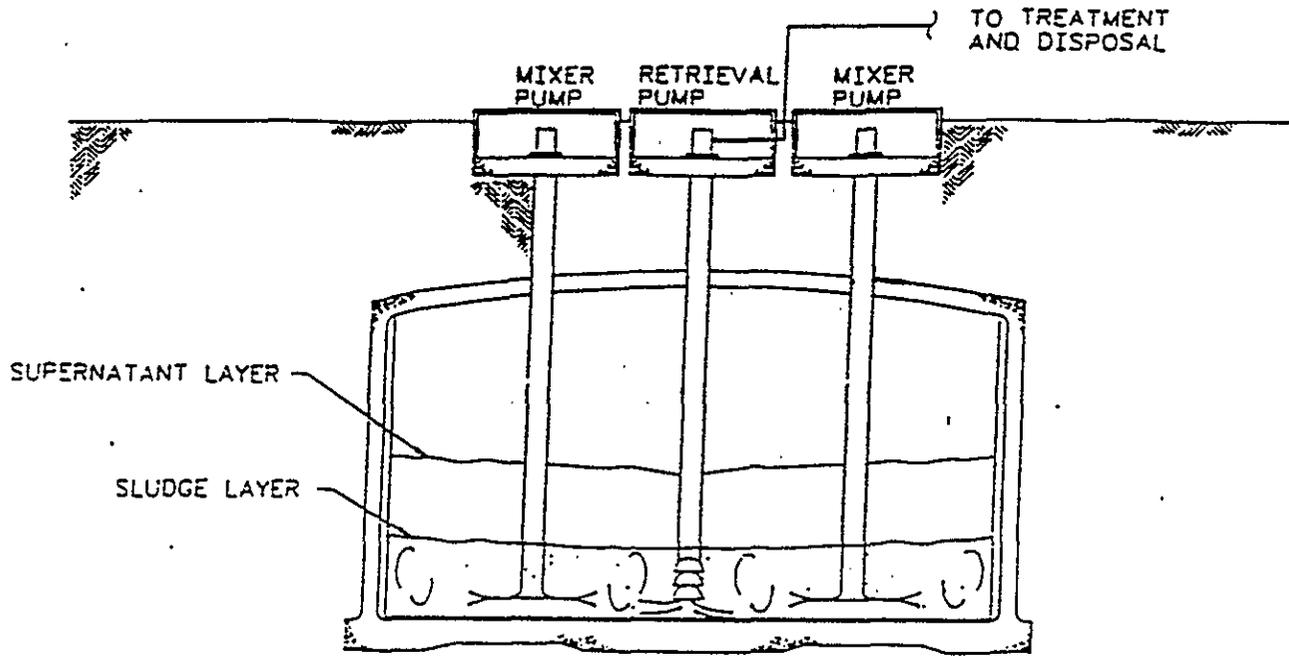
DST hydraulic retrieval carries two options: mixer pumps and sluicers. Mixer pumps use a submerged jet to mobilize material through the mechanisms of erosion and fluid shear. Sluicers (or monitors, as they are called in the mining industry) use a high volume liquid jet impinging the waste's surface to mobilize material through kinetic impact and erosion.

6.3.2.1 Mixer Pumps. The mixer pump performs two key tasks with respect to waste mobilization. It both generates the hydraulic pressure to feed integrally mounted jets to mobilize waste, and it also recirculates liquid within the tank to maintain suspension of solid waste until pumped. For the DST application, it is assumed four mixer pumps are used with a centrally mounted slurry pump to transfer the waste from the tank (Figure 6-7). Because of the difficulty expected in using mixer pumps to mobilize and remove the tank heel, small sluicers tailored to heel removal will be integrated with all mixer pump operations.

In addition to retrieval, mixer pumps may also be used for Waste Separations as an option called in-tank sludge washing. Because much of the DST sludges and solids are soluble, the recirculating action of the mixer pump can perform the dissolution or 'washing' of the waste material. This feature of mixer pumps for in-tank washing is discussed further in Chapter 7.0. In this section, however, the evaluation of mixer pumps is made solely on the basis of satisfying retrieval requirements.

6.3.2.2 Sluicing. As noted in Section 6.1.1, the sluicing of tank sludges is a proven technology successfully applied at the Hanford Site. Following the removal of supernatant via transfer pumps to uncover the sludge/solids layer, DSTs would be sluiced similar to past sludge removal campaigns. The equipment and methods would be identical to those employed for SSTs.

Figure 6-7. Hydraulic Retrieval—
Double-Shell Tank Mixer Pump.



(DST) RETRIEVAL SYSTEM

As with mixer pumps, some sludge washing occurs during the recirculation of liquid to the sluicers, but this effect may not preclude the use of mixers for sludge washing.

F3.2 TECHNOLOGY SELECTION

This section of the appendix covers the screening of retrieval technologies drawn from many of the previously noted documents, the TWRS technology working group and other sources, to select a group of options for evaluation in the report. The effort is summarized in Figure F3-1. The screening is not meant to be a comparative evaluation, nor is it based on developed performance or cost data. Rather it is based on a general assessment of the given technologies in light of noted functions and requirements, assumptions and key considerations.

F3.2.1 Retrieval and Transfer Functions

The retrieval and transfer functions are introduced in Chapter 1.0 of the Technology Options Report. Figure F3-2, sheet 1, Tank Waste Retrieval and Waste Transfer Flow Diagram, illustrates their relationship to the other functions of the TWRS. Figure F3-2, sheet 2, integrates retrieval and transfer with the closure related functions apart from the TWRS mission. The functions are defined as follows:

- **Retrieval**—The removal of waste from an UST to the degree necessary to satisfy governing regulatory requirements. Debris intermingled with the waste is not necessarily considered part of the function but its retrieval could be deemed essential or incidental to the satisfactory completion of the task.
- **Transfer**—The transfer of UST waste from the tank site to suitable storage and/or transfer to waste separations. The transfer of debris is considered incidental to the primary transfer function.

Most of the previously noted studies and reports view waste retrieval as a standalone task. The *Tank Waste Technical Options Report* views retrieval and transfer as integrated functions within an overall tank farm closure strategy. Thus, efforts were made to focus on concepts and apply technologies which could both stand alone and be integrated to the benefit of both retrieval and closure functions.

Because closure criteria were (and remain) undefined, these concepts embraced a broad set of closure scenarios from in situ stabilization of tanks and contents, to removal of tank contents, tank structures, and surrounding soils. However, with closure no longer within the scope of the TWRS mission, some of the technologies may appear inappropriate, particularly those suited to an integrated retrieval/closure strategy. This issue should be noted as the appendix is read.

A number of the previously noted documents carry retrieval functional hierarchies, breakdowns, and analyses. Various performance criteria and requirements and constraints are identified as well. And, of course, a wide range of conclusions and recommendations are presented as a result. In the *Preliminary Report of the Retrieval Systems Assessment Team* (Bustard et al. 1992) a number a spread sheets were developed which attempt to quantify and summarize the wide range of findings presented in these past works.

The most notable difference between these past efforts and the current Report is the framework used to couple the retrieval and transfer technology options to an overall TWRS strategy.

F3.2.2 Requirements, Assumptions, and Considerations

The original functions and requirements document (Boomer et al. 1990) was used as the basis for narrowing the range of technology options considered. A more recent functions and requirements document (Lowe 1993), prepared to support TWRS, follows an alternate approach, but in the area of retrieval and transfer many of the constraints and bounding criteria remain unchanged; i.e. Tri-Party Agreement milestones, DOE orders, and environmental regulations. Thus, the impact on the technology selection appears minimal.

Assumptions were also required to enable the comparison of options, to develop cost estimates, performance evaluations, etc. In some cases these are supported only by engineering judgment without a strong technical basis.

Many of the documents noted in Section F3.1, particularly those written after 1989, identify retrieval requirements and similarly develop assumptions. Those found in *Single-Shell Tank Waste Retrieval Requirements* (Krieg 1990) were used as a basis for the work done in this appendix. Notable additions and exceptions are described in the following paragraphs. These coupled with the previously noted functions and requirements formed the basis of the technologies selected for the report.

F3.2.2.1 Schedule. Following the Tri-Party Agreement Milestone M-09, it is assumed that all SSTs are closed by the end of FY 2018. The start of production retrieval is consistent with another Tri-Party Agreement milestone M-08 and start of FY 2005. As the baseline duration for retrieval of all SST farm, 10 years was chosen.

It is also assumed that closure activities (following retrieval) will begin by the start of FY 2008. This will allow approximately 10 years to perform closure of the tank farm sites, with three years unencumbered by retrieval activities.

As a schedule basis for DST retrieval it is assumed that retrieval will take 5 years without a defined start or completion date. No credible DST retrieval schedule has been developed as of this writing. Priority lists have been prepared, but no negotiated milestones have been finalized with respect to DST retrieval or closure.

F3.2.2.2 Production Rates. Production rates of the retrieval and transfer functions are assumed to be constrained by the above schedule dates and interfaces with downstream separations and closure functions. The overall campaign retrieval rate for SST farms is assumed to be 64 m³/day (16,900 gal/day) based on a total operating efficiency of 60 percent. For DST farms the campaign retrieval rate is 84.9 m³/day (22,410 gal/day) based on 60 percent total operating efficiency.

These values represent overall campaign rates and do not reflect individual unit production rates. As an average rate there is no distinction between the waste form retrieved; slurry, supernatant, sludges or salt cake. The retrieval rates for a given retrieval technology and waste form will be found with the technology descriptions in Sections F4.0 and F5.0. Also note that any debris removal associated with waste retrieval activities will be performed without penalty to these average retrieval values.

F3.2.2.3 Separations Interface. All retrieved waste which is transferred to the separations function will be conditioned to a pumpable form and blended to a 5M sodium solution carrying no greater than 10 percent solids. Particle size will be limited by total solids content and settling velocities which is not considered a major constraint.

F3.2.2.4 Closure Interface. It is assumed that following retrieval, closure activities will proceed without any impact to ongoing retrieval or transfer functions. If necessary, closure activities will be conducted simultaneously with retrieval operations within the same farm.

F3.2.2.5 Universal Application. A wide variability of waste forms and properties are known to exist in the USTs. Different retrieval technologies and systems tailored to specific waste forms would add considerable complexity to the retrieval mission, particularly where multiple forms exist in the same tank. Therefore it is important that the technology(s) selected are universally applicable to all USTs. It is assumed that any variations in tank waste properties or tank conditions are accommodated to acceptable degrees by any of the technology options to be carried in the report. This assumption does not apply to specific 'tools' tailored to a specific waste form. In this context, the 'tool' is considered only an element of a broader or baseline retrieval technology or system.

Waste tank decontamination and tank waste characterization are not considered part of the waste retrieval task. Technologies and systems developed to perform these tasks are not to be considered 'retrieval systems.' Though it may be desirable to integrate these tasks into the retrieval mission, for a variety of reasons they remain outside the retrieval function. Waste tank decontamination is tied to closure and is driven by the determination of acceptable waste residual levels. Characterization is driven by established Tri-Party Agreement agreements and other regulations.

F3.2.2.6 Technical Maturity. Because of the methods used in developing cost and schedules used in the evaluation, candidate technologies must be developed beyond the conceptual or idea stage to be considered for the report. As a practical consideration, if a technology does not have a sufficient technical basis from which a credible process or

equipment description can be prepared and estimated, it is not considered. Selected technologies introduced as enhancements to primary or baseline technologies must also be viewed from the maturity standpoint, particularly if it's key to the success of the supported baseline technology.

Technical maturity is also used as an evaluator in Section F9.0. But, in that application, it is used as a tool for evaluation rather than screening.

F3.2.2.7 Complex Infrastructure. Many candidate technologies for waste retrieval are considered mature from an industrial standpoint. However, their application to production within the radioactive and hazardous waste UST environment may be new and unproven. Where technologies are expected to be exceedingly complex and/or require significant infrastructure, without compensatory payback through performance, they are not considered for evaluation.

F3.2.3 Candidate Technologies For Retrieval

The descriptions of technologies and discussion of the pros and cons can be found in the TWRS National Technology Workshop report (WHC 1992) with more detailed information on some concepts found in *Single-Shell Tank Waste Retrieval System Concept Review* (Wellner 1991) and other predecessor documents.

In applying the screening process, a distinction was first made between retrieval systems in terms of the original functional breakdown of the mission. A system which could be adopted to both retrieval and closure functions is considered a multi-purpose system. While a system which could only be applied to the retrieval function is called single purpose. The current TWRS mission presently emphasized the single-purpose pathway. Figure F3-1, Retrieval Technology Options, identifies the technologies carried in the report, those rejected, and notes the primary basis for rejection.

Those selected for the report are the following:

- Multi-purpose technologies
 - Large robotic manipulator arm (SSTs only)
- Single-purpose technologies
 - Long reach robotic manipulator arm (SSTs only)
 - Sluicing with slurry pump removal with/without barrier enhancement
 - Mixer pumps with pump retrieval (DSTs only).

Additional technologies are illustrated in Figure F3-1 as sub-functions of the selected baseline technologies noted above. They represent an array of technologies which, as a group, are essential to the satisfactory performance of the baseline technology, but note that no 'one' technology is singularly critical. The current viability of these technologies varies considerably and the listing is not intended to be all inclusive. Many of these are described in detail in the above references and considerable detail in the following sections.

F3.2.4 Candidate Technologies for Transfer

Much of the work done in previous studies and workshops did not view waste transfer as a separate, standalone function. It was considered a sub-function which was typically satisfied through pumping technologies, i.e., trash pumps, slurry pumps, piston pumps. In many retrieval concepts, little mention is made of transfer at all. The prevailing presumption was that tank waste already was, or could easily be, conditioned into a pumpable product.

For the report, which views waste transfer as a separate function, three technologies were initially identified for screening: container, slurry (pump), and conveyor transfer. Based on the general requirements and constraints noted in Sections F3.2.2 it was concluded that conveyor transfer would be most difficult to apply universally to all waste forms and exceedingly complex in implementation.

Conveyor technologies suitable for solids such as belt, bucket, vibratory and differential friction conveyors, were found unsuitable for sludges and more dilute wastes. Few conveyor technologies were found suitable for sludges and more dilute wastes. Bucket conveyors and variations of pressure/vacuum conveyors appeared to be marginally acceptable for some sludges, but were not considered practical for the broader range of 'wet' solids or more dilute wastes.

In general, it was thought that without significant waste conditioning, i.e., delumping, evaporation, drying, size classification, and reduction, conveyor transfer could not satisfactorily handle the waste forms expected. But, more importantly, the complexity of implementing a conveyor system transporting high exposure, hazardous wastes for the distances expected appeared as insurmountable obstacles. For these reasons, conveyor transfer was dropped from further consideration and container and slurry transfer remain as the technologies carried in the report.

F3.3 RETRIEVAL AND TRANSFER FUNCTION ELEMENTS

The retrieval and transfer functions are comprised of process elements which constitute the integrated retrieval and transfer tasks. These process elements are illustrated in Figure F3-2, which is a block diagram joining the process elements by applying the decision logic of various retrieval options. The following section describes the elements in detail and the various decisions points associated with the option logic.

F3.3.1 Site Preparation

Regardless of the baseline retrieval options selected, some level of tank site preparation will be necessary. If significant facility infrastructure must be constructed to support retrieval, it is likely that existing surface and sub-surface structures, i.e., pits, encasements, electrical services, will require removal prior to construction. The process will produce waste which must be classified, properly packaged, and stored and/or disposed.

F3.3.2 Support Services

The retrieval operation will require significant service support in the form of basic utilities and as-low-as-reasonably achievable (ALARA) controls i.e., decontamination, ventilation, shielding, and confinement. To provide these services for some retrieval options may require substantial support facilities. Needed services may also require additional access to the tanks in the form of additional and/or larger penetrations and risers for ventilation, instrumentation, and monitoring.

F3.3.3 Tank Penetrations

In addition to satisfying basic service requirements, the selected baseline retrieval technology may also impose modifications to the tank dome. Large penetrations may be required to handle retrieval arms or multiple penetrations may be required for sufficient tank access for a retrieval unit. Debris materials generated during the dome modifications would be classified, packaged, stored and/or disposed or placed in the tank for disposition at a later time with other in-tank waste.

F3.3.4 Control System

A control system commensurate with the complexity of the baseline retrieval unit will be used. The system provides a hierarchy of controls which may range from basic manually directed functions to fully automated sequences and integration with balance of plant services.

F3.3.5 Maneuvering System

The maneuvering system provides for the deployment and in-tank movement of waste mobilization devices. Single-purpose systems, such as mixers and sluicers, have no need for a maneuvering system while maneuvering is integral with all arm-based systems. In this process element, rotation or single-degree movement of nozzles is not considered 'maneuvering.'

F3.3.6 In-Tank Debris

Debris in the form of failed equipment, miscellaneous hardware, tools, and fuel assemblies located in the USTs will be encountered during retrieval activities. Arm-based systems will have the maneuvering ability to deal with debris (i.e., displace, remove). Sluicing systems must rely on other systems or strategies in dealing with debris. An exceedingly small volume of this material exists.

F3.3.7 Barriers

Barriers offer the capability to arrest or slow the movement of soil borne contaminants to the groundwater. Retrieval systems which could precipitate the release of contaminants through tank leaks to the groundwater, may require barriers to achieve acceptable environmental performance.

F3.3.8 In-Tank Conditioning

Waste must be mobilized and placed in a form or condition such that it can be removed or transferred from the tank. Methods and hardware to accomplish this are tailored to the various waste forms.

F3.3.9 In-Tank Transfer

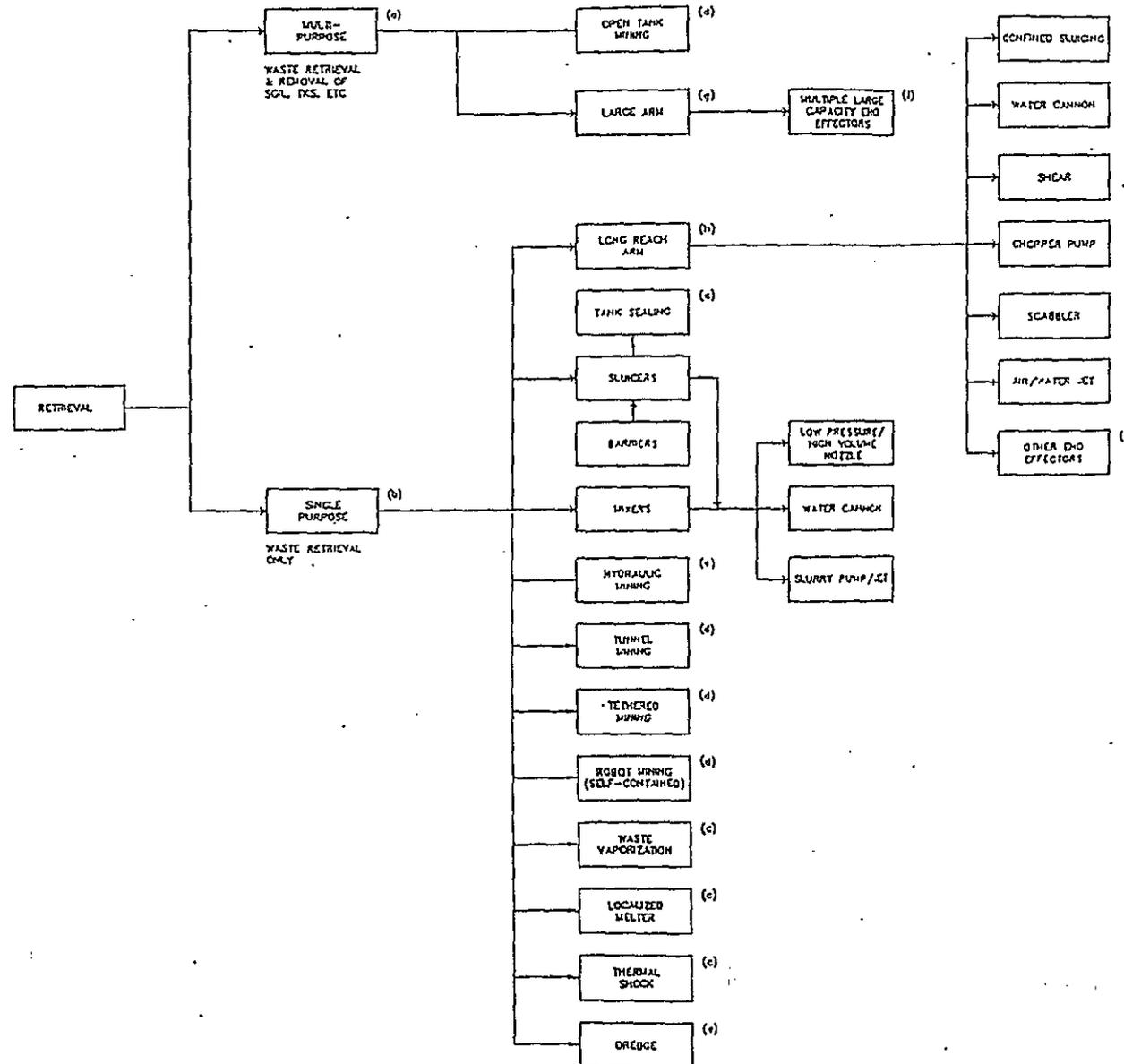
Following mobilization of the waste and its conditioning, if necessary, it must be removed from the tank. The methods to accomplish this are generally limited by the waste form and rely on particular waste properties, i.e. size, density, and percent liquid. Waste transfer following removal from the tank, is similarly influenced by the properties of the retrieved waste. Generally a pumpable waste would favor slurry transfer; a solid or debris waste would favor container transfer.

It should be noted that only slurry transfer is recognized as the interface with the downstream separations function. Though solid waste may be transferred from the tanks by containers or casks it must be conditioned either locally at a farm site or central location and ultimately transferred as a slurry.

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RETRIEVAL TECHNOLOGY OPTIONS

Figure F3-1. Retrieval Technology Options.



LEGEND:

OPTION EVALUATED IN CHAPTER 6.

OPTION NOT CONSIDERED IN CHAPTER 6.

NOTES:

- (a) CONFINEMENT TYPICALLY PROVIDED BY FACILITY CONCEPTS WHICH ENCLOSE THE ENTIRE SURFACE AREA ABOVE A TANK.
- (b) CONFINEMENT TYPICALLY PROVIDED BY THE TANK ITSELF AND ENCLOSURES AROUND OPERATING EQUIPMENT LOCATED IN TANK RISERS OR PENETRATIONS.
- (c) BASIC RESEARCH AND DEVELOPMENT REQUIRED BEFORE THESE TECHNOLOGIES CAN BE FURTHER EVALUATED.
- (d) MECHANICAL AND CONTROL COMPLEXITY REQUIRED IN ADAPTING TECHNOLOGIES TO THE RADIOACTIVE WASTE ENVIRONMENT DEFEAT PERCEIVED BENEFITS.
- (e) THESE TECHNOLOGIES ARE DEVELOPED BUT FOUND TOO LIMITED OR TOO COMPLEX TO APPLY FOR GENERAL RETRIEVAL USE; MAY BE SUITABLE FOR LIMITED APPLICATION IN SOME FORM.
- (f) DIO EFFECTORS USE DEMONSTRATED COMMERCIAL TECHNOLOGIES FOR WASTE MOBILIZATION; MUST INTERFACE WITH MANEUVERING AND TRANSFER SYSTEMS.
- (g) LARGE CAPACITY, SHORT REACH ARM USED FOR WASTE RETRIEVAL AND TANK SOL, PUMP, ETC. REMOVAL; CAPABLE OF RELATIVELY HIGH RETRIEVAL PRODUCTION RATES. MULTIPLE DIO EFFECTORS USED FOR GENERAL TASKS.
- (h) LONG REACH ARM USED FOR WASTE RETRIEVAL ONLY; LIMITED CAPACITY AND CAPABILITY IN HANDLING BY TANK HARDWARE AND OTHER TASKS. MULTIPLE DIO EFFECTORS USED FOR SPECIFIC TASKS.

Figure F3-2. Tank Waste Retrieval and Waste Transfer Flow Diagram. (sheet 1 of 2)

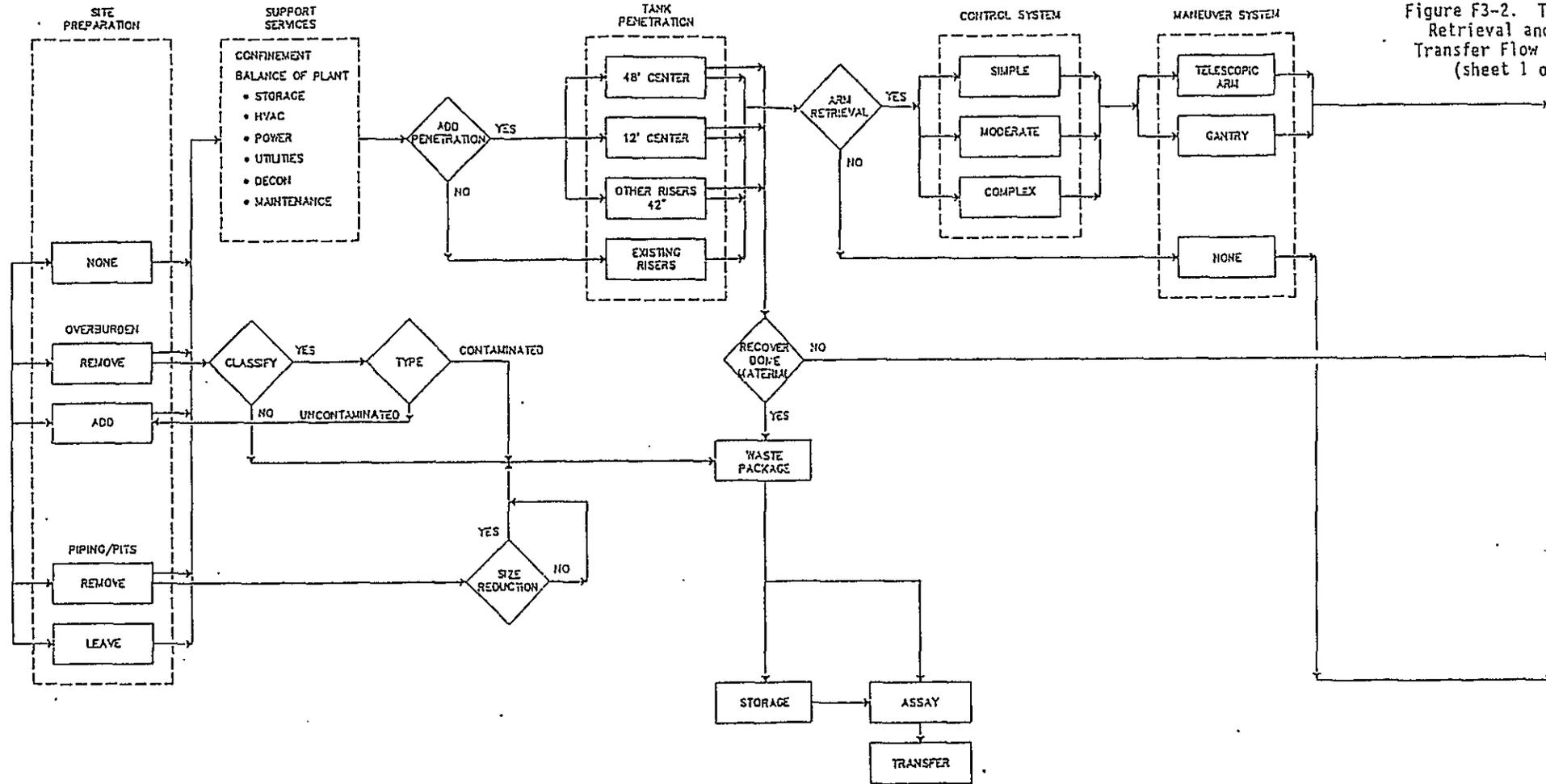
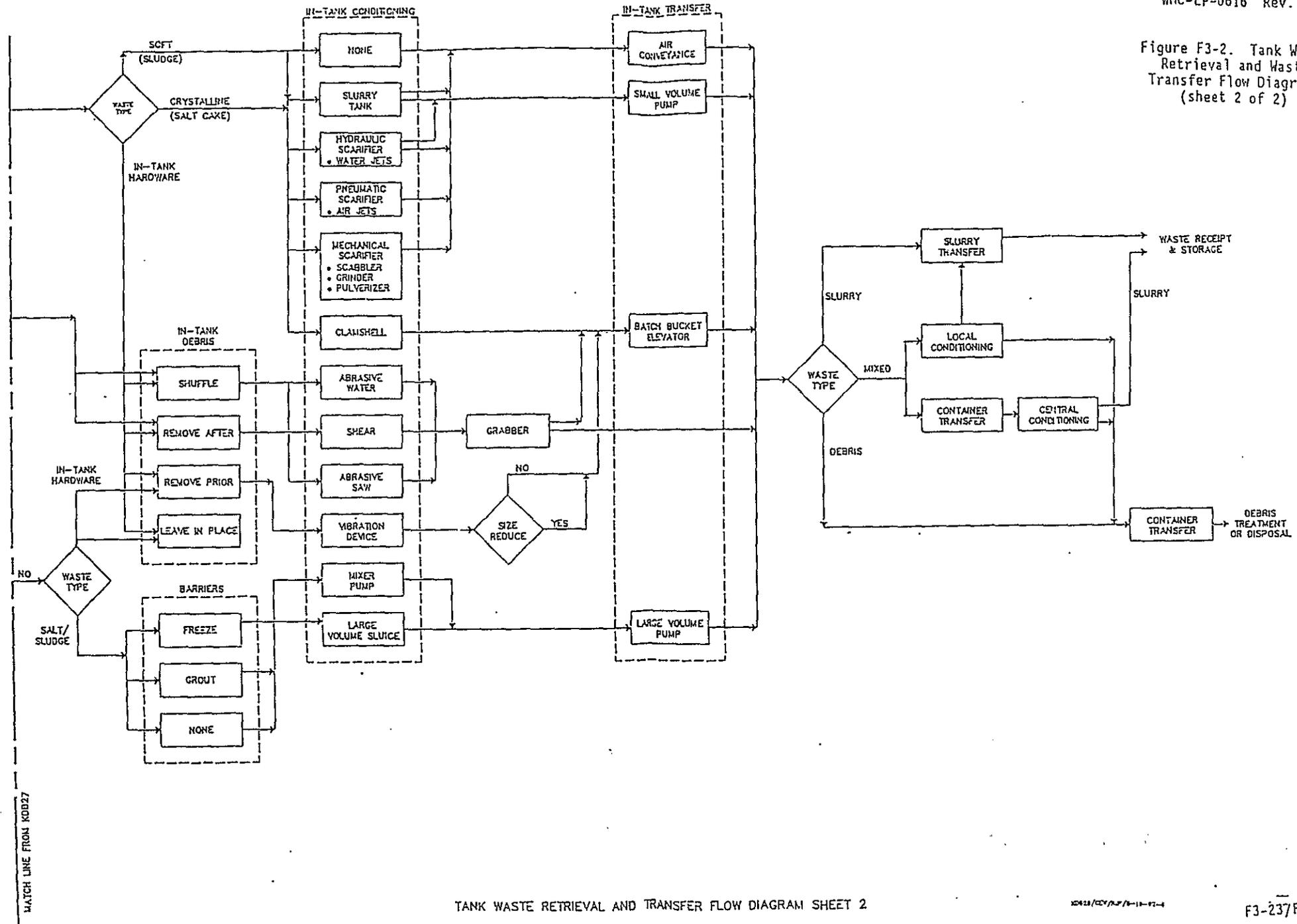


Figure F3-2. Tank Waste Retrieval and Waste Transfer Flow Diagram. (sheet 2 of 2)



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APPENDIX C

EXCERPTS FROM TANK WASTE TECHNICAL OPTIONS REPORT
WHC-EP-0616, REV. 0, 1993
(SEPARATIONS PRETREATMENT)

7.1	SELECTION OF SEPARATIONS TECHNOLOGY OPTIONS
G1.1	SELECTION OF SEPARATIONS TECHNOLOGY OPTIONS
G17.0	REFERENCES

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7.1 SELECTION OF SEPARATIONS TECHNOLOGY OPTIONS

This section describes the selection of separations technology options for evaluation. The separations technology options discussed in this chapter are made up by combination of individual unit processes to attain the overall process desired. The individual unit processes were initially identified by literature reviews of radionuclide separations processes. Unit processes were then selected from the identified processes based on technology demonstration status.

7.1.1 Identification of Unit Separations Processes

Unit radionuclide separations processes are shown in Figure 7-2, Separations Technology Processes. Unit processes used in the separations technology options are identified by the heavy lines and are discussed in Sections 7.2.1 through 7.2.11, and Appendix G. Unit processes not used in separations technology options are identified with light lines and a note explaining the reason for rejection. More detailed discussions of the rejected technologies with references are provided below and in Appendix G.

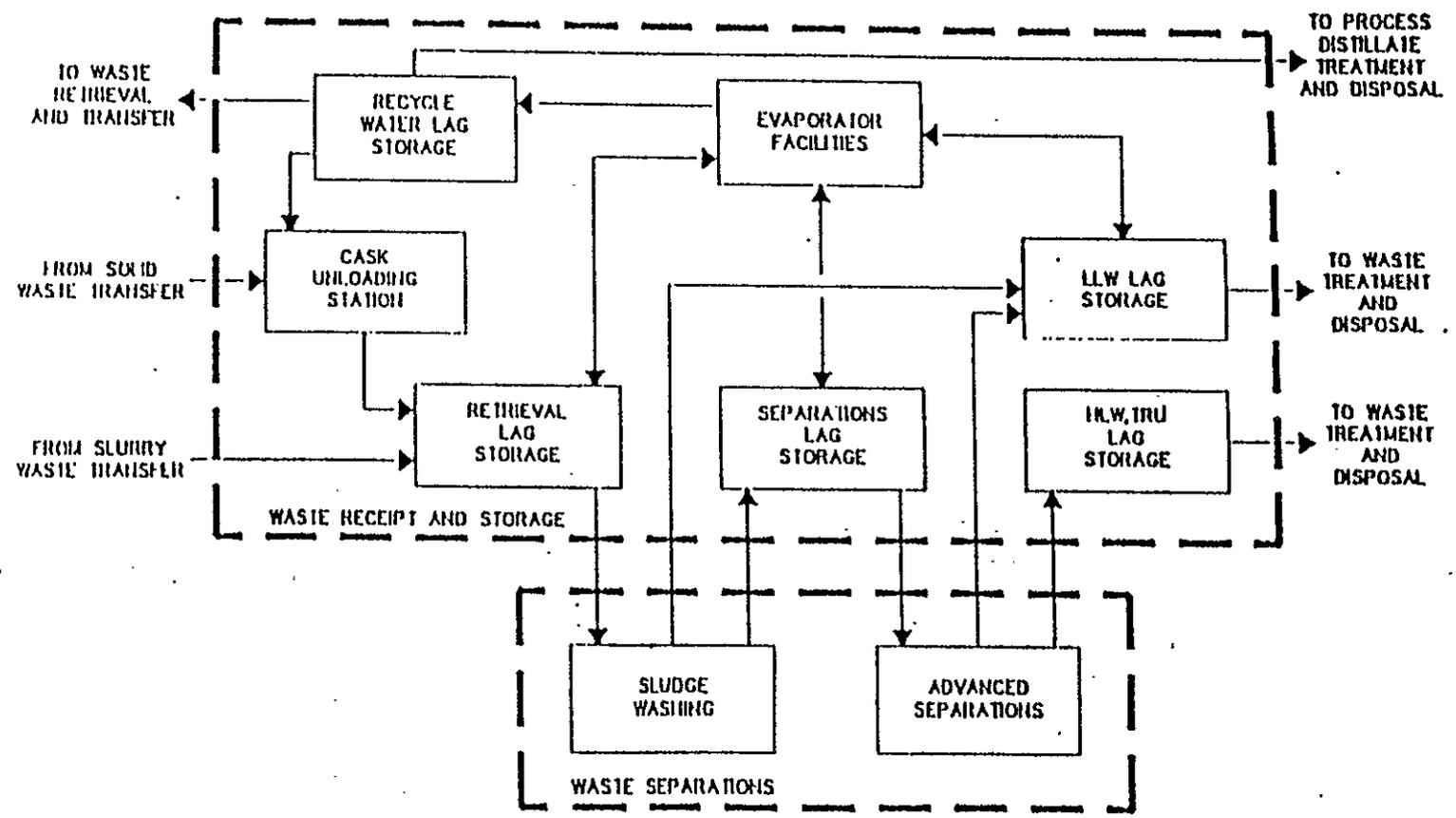
The organization of Figure 7-2 follows treatment of tank wastes with pyrochemical, aqueous acidic, or aqueous alkaline processes. Following are the criteria for selection or rejection of the aqueous processes shown in Figure 7-2. Additional details are provided in Appendix G.

7.1.1.1 General Criteria. For plant-scale nuclear applications, continuous countercurrent liquid-liquid solvent extraction processes, when available, are generally preferred over ion exchange, precipitation or extraction chromatographic processes. Over 40 years of successful experience in the United States and elsewhere demonstrate that liquid-liquid solvent extraction processes can be operated on a large scale to accomplish, routinely and satisfactorily, high throughput nuclear separations in well-established and readily available contacting equipment.

In those cases where solvent extraction technology is either not available or, for some reason, not desirable; fixed-bed ion exchange processes are usually preferred over either precipitation or extraction chromatographic processes. Fixed-bed load-wash-elute ion exchange processes were successfully used on a plant-scale at the Hanford Site to separate megacurie amounts of ^{137}Cs . Precipitation processes also have been used at Hanford for separation of plutonium, ^{137}Cs , ^{90}Sr , and fission product rare earths.

Precipitation processes are batch rather than continuous processes; simple batch precipitation processes typically are incapable of removing >99 percent of a particular radionuclide or group of radionuclide and also do not provide acceptable decontamination of separated radionuclides from contaminants. Extraction chromatographic processes are useful

Figure 7-1. Waste Receipt, Storage, and Separations Flow Schematic.



ALB1/CEW/0-7-82-9

SEPARATION TECHNOLOGY OPTIONS - SHEET 1

LEGEND

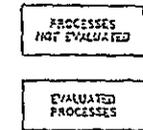
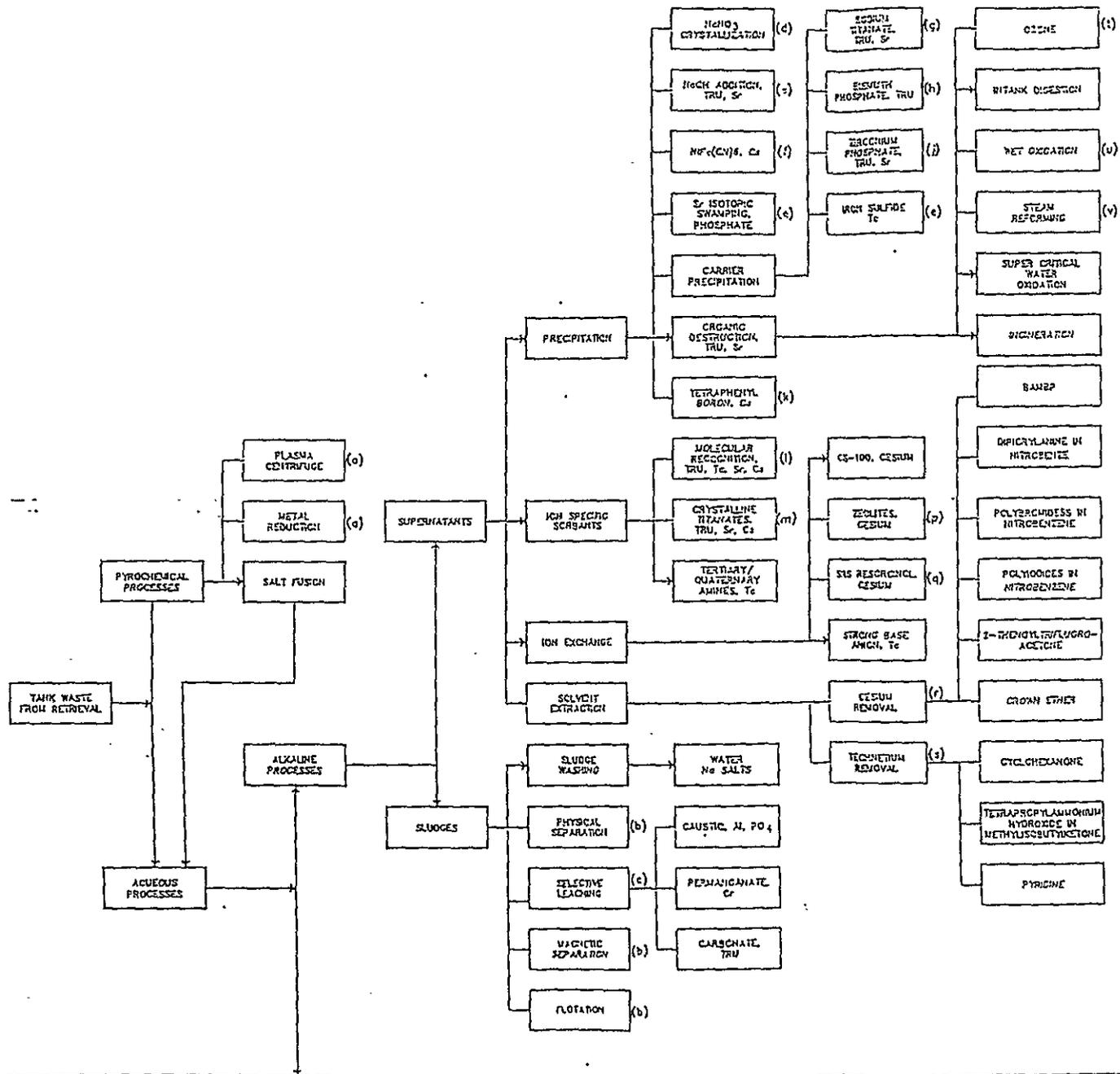


Figure 7-2. Separations Technology Processes. (sheet 1 of 2)



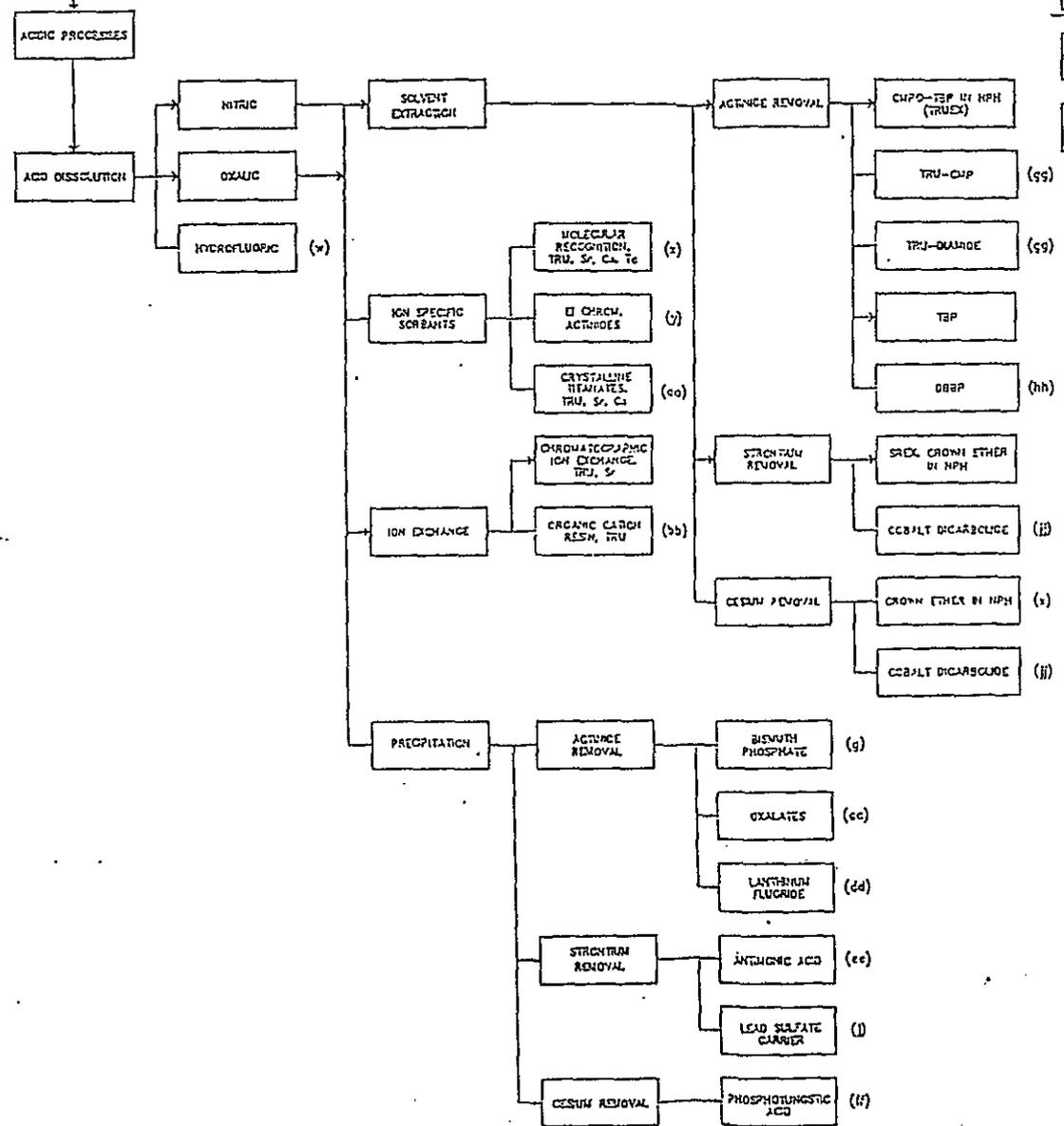
NOTES

- (a). APPLICABILITY IS UNCERTAIN-UNITED DEVELOPMENT.
- (b). UNTESTED FOR REMOVING SELECTED SLUDGE COMPONENTS.
- (c). LIMITED LABORATORY TESTS-APPLICABILITY IS UNSURE.
- (d). A CONCENTRATION METHOD, NOT REMOVAL.
- (e). RELATIVELY UNTESTED FOR HANFORD ALKALINE SUPERNATANTS.
- (f). MUST CAREFULLY CONTROL AIR FERROCYANIDE IS SAFETY ISSUE.
- (g). UNLIKELY NOT EFFECTIVE FOR COMPLEXED Sr AND TRU. MUST DESTROY COMPONENTS FIRST.
- (h). GENERATES EXCESS WASTE, INCREASING CANISTERS AND VOLUME.
- (i). GENERATES EXCESS WASTE, MAKES GELATINOUS PRECIPITATES.
- (j). HAZARDOUS CHEMICAL BYPRODUCT MUST BE DESTROYED.
- (k). LIKELY APPLICABLE FOR Cs AND Te BUT ION-EXCHANGE MORE THOROUGHLY TESTED; COMPONENTS MAY INTERFERE WITH Sr AND TRU.
- (l). COMPETITIVE WITH ION-EXCHANGE FOR Cs BUT WOULD ADD 10X VOLUME; COMPONENTS MAY INTERFERE WITH Sr AND TRU.
- (m). ZEOLITE CHEMICALLY UNSTABLE, INCREASE GLASS VOLUME.
- (n). COULD REPLACE Cs-100; WOULD NOT CHANGE FLOWSHEET SIGNIFICANTLY.
- (o). PHASE SEPARATION DIFFICULTIES AND TOXIC SOLVENTS.
- (p). RELATIVELY UNTESTED; MUST USE HAZARDOUS OLUENT; EMULSIONS A PROBLEM WITH ALKALINE SOLVENT EXTRACTION PROCESSES.
- (q). COMPONENTS NOT COMPLETELY DESTROYED, REQUIRES SIGNIFICANT VOLUMES OF OZONE; PROCESSING IN-TANK PROBABLY NOT PRACTICAL.
- (r). MAY BE COMPETITIVE WITH SLOW; FURTHER TESTING NEEDED.
- (s). MAY BE SED AGGLOMERATION WITH HIGH SCODIUM WASTE.
- (t). EXCESSIVE SLOUGH VOLATILITY MAY PLUG OFF GAS TRAP.
- (u). MINIMAL TESTING-POSSIBLE FUTURE PAYOFF.
- (v). TESTING NEEDED-DESIGNED FOR ANALYTICAL PURPOSES.
- (w). REQUIRES ADJUSTMENT TO SLIGHTLY ACID pH.
- (x). INTERFERENCE WITH Fe AND OTHER CATIONS; ANIONIC RESINS ALSO NEEDED FOR Pu AND U.
- (y). MULTIPLE STEPS NEEDED TO REDUCE CONCENTRATIONS OF ALL TRU ELEMENTS TO < 100 nCi/g BY ACIDIFIED WASTES.
- (z). CUMBERSOME BATCH PROCESS; INCREASES GLASS VOLUME.
- (aa). DIFFICULT TO RECOVER PRECIPITATE, LOW RECOVERY.
- (ab). REQUIRES RELATIVELY HIGH Cs CONCENTRATION, THIS REQUIRES ISOTOPIC DILUTION; INCREASE IN CANISTERS.
- (ac). LIMITED TESTING COMPARED TO TRUCK PROCESS. FURTHER TESTING REQUIRED.
- (ad). DIFFICULT TO ADEQUATELY EXTRACT ALL ACTINIDES AT SINGLE ACIDITY.
- (ae). HAZARDOUS OLUENT-NOT TESTED BY US.

MATCH LINE TO DRAWING ALB139

MATCH LINE FROM DRAWING AL3133

SEPARATION TECHNOLOGY OPTIONS - SHEET 2



LEGEND

PROCESSES NOT EVALUATED

EVALUATED PROCESSES

NOTES

FOR NOTES SEE DRAWING AL3133

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Figure 7-2. Separations Technology Processes. (sheet 2 of 2)

AL3133/AL3/06/10-11-1

for small volume highly specialized separations, e.g., trivalent actinides from trivalent rare earths, but because of capacity and selectivity limitations, are not particularly useful for handling large volumes of feed.

7.1.1.2 Separation of Radionuclides from Acidic Wastes.

TRU Elements and Technetium-99--For reasons already stated, liquid-liquid extraction processes are preferred over precipitation (e.g., oxalates or fluoride) processes or extraction chromatographic processes for separation of TRU elements from acidified wastes. Bifunctional extractants, e.g., carbamoylmethylene phosphine oxides (CMPO/ or diamides) are much preferred over monofunctional reagents such as dibutylbutylphosphonate because they efficiently extract Am^{3+} as well as +4 and +6 actinides from strongly acidic, i.e., $>0.5M$ HNO_3 feeds. For several reasons, e.g., commercial-availability, ability to co-extract ^{99}Tc , decontamination potential, etc., one particular CMPO, namely octylphenyl-N, N-diisobutylcarbamoylmethylphosphine oxide, is the currently preferred TRU element extractant.

Strontium-90--Processes which effectively and selectively remove ^{90}Sr from strongly acidic solutions are difficult to devise. The currently best available technology appears to be the SREX process, a solvent extraction process employing as the extractant a commercially-available crown ether diluted with n-octanol or TBP and NPH. The SREX process is highly selective for Sr^{2+} over a wide range of feed acidities; only Ba^{2+} co-extracts to any extent. Dilute NH_4OH solutions readily strip Sr^{2+} from the solvent.

Two other processes are potentially available for separating ^{90}Sr from acidic media. One of these is the dicarbolyde solvent extraction process long studied by both Russian and Czechoslovakian scientists. According to these investigations, dicarbolydes effectively and selectively extract both Cs^+ and Sr^{2+} from acidic media provided a polyglycol is added to the feed. A major, perhaps insurmountable, disadvantage of the dicarbolyde extraction process is that the required diluents are nitrobenzene or chlorinated benzenes. Such toxic diluents are no longer acceptable for use in U.S. nuclear separation plants.

Crystalline polyantimonic acid also effectively and selectively sorbs ^{90}Sr from nuclear acidic wastes. The principal disadvantage to this ion exchanger is that no single and inexpensive way of eluting sorbed ^{90}Sr is known. There are also concerns about the commercial availability of plant-scale quantities of crystalline polyantimonic acid.

Cesium-137--A need to remove ^{137}Cs from acidic waste solutions has not been established. If such removal is required from some acidic solutions, the simplest procedure is to adjust the acid waste to pH 9-10, after prior removal of TRU elements and ^{90}Sr , and use well-known ion exchange materials and procedures for removal of ^{137}Cs .

Subject to the limitations discussed earlier a batch precipitation of cesium phosphotungstate (PTA) could be used to remove about 95 percent of the ^{137}Cs directly from the acid waste. Alternatively, it may be feasible to remove ^{137}Cs from the acid waste by

means of the cesium-strontium extraction process. The latter is a solvent extraction process currently just under development at the Argonne National Laboratory; the extractant is a commercially-available crown ether. Crystalline sodium titanate has also been reported to sorb ^{137}Cs from acidic media. Applicability of this solvent to Hanford Site acid wastes needs to be determined.

7.1.1.3 Separation of Radionuclides from Alkaline Wastes.

Technetium-99—The classic and preferred way of removing ^{99}Tc from alkaline waste solutions is to selectively sorb it, as TcO_4^- , on a strong-base organic ion exchanger. Sorbed ^{99}Tc can be eluted with 6M HNO_3 solution.

Various organic compounds, e.g., cyclohexanone, pyridine, tetra propylammonium hydroxide, are known to extract ^{99}Tc from alkaline wastes. Of these reagents, cyclohexanone appears most promising and has been studied on a bench-scale with actual Hanford wastes. Further work including pilot-plant scale tests with the cyclohexanone extraction process are required to determine the extent of emulsion problems in solvent extraction of the alkaline waste solution.

Cesium-137—Organic cation exchange resins were employed very successfully at Hanford on a plant-scale for many years to remove ^{137}Cs from alkaline wastes. Such technology using newer resins, e.g., CS-100 or a resorcinol-based exchanger developed at the Savannah River Site is still the preferred technology for removing ^{137}Cs from alkaline tank wastes.

Alternative methods for removing ^{137}Cs from alkaline solutions all appear to have disadvantages compared to well-established ion exchange technology. Thus, various precipitation agents; e.g., tetraphenyl boron, nickel ferrocyanide, etc., must all be applied on a batch basis and, in a single precipitation step, may not give required yields. Furthermore, downstream treatment of the Cs-laden precipitates involves potential safety hazards. Candidate solvent extraction processes employing such extraction as BAMBIP, dipicrylamine, polybromides, and crown ethers have not either been fully developed or require use of toxic diluents such as nitrobenzene.

Destruction of Organic Complexants—Leading candidates for organic destruction include heat and digest, supercritical water oxidation (SCWO), and incineration. In-tank digestion will degrade components that result in hydrogen generation; (e.g., HEDTA). Incineration and SCWO will degrade organics to $\text{CO}_2 + \text{H}_2\text{O}$, and will also result in precipitation of ^{90}Sr and TRU elements. Other candidates, including wet oxidation and steam reforming, may be competitive with SCWO but need further development.

7.1.2 Combination of Unit Processes Into Technology Options

The unit processes selected on the basis of technology status are combined into five basic processing options with different levels of separations performance.

1. In-Tank Sludge Washing—Transfer waste to double-shell tanks (DSTs) where supernatant is decanted and sent to onsite disposal. Wash the remaining solids and then decant the soluble components to onsite disposal. Treat the washed solids for offsite disposal. Two levels (A and B) of radionuclide removal are defined.
2. Sludge Washing—Separate solids or sludges from supernatant liquids and wash solids with dilute caustic to remove soluble salts. Treat the insoluble solids for offsite disposal. Four levels (A, B, C, and D) of radionuclide removal are defined.
3. Solvent Extraction (TRUEX) Processing—Separate solid and liquid (sludge washing) and further reduce waste solids requiring HLW treatment by acid dissolution of the sludges. The TRUEX process results in an approximate factor 3 reduction in volume of glass for offsite disposal. Transuranic components are removed from the acidic waste for treatment and offsite disposal. Four methods or levels (A, B, C, and D) of supplemental radionuclide removal are defined.
4. Clean—Separate solid and liquid fractions and further reduce waste solids requiring HLW treatment by (a) caustic and multiple acid leaches of the sludges, (b) extraction of radionuclides from aqueous solutions, and (c) separate inert elements from recovered radionuclide fractions. The goal of the Clean process is to reduce HLW to less than 1,000 canisters, produce a Nuclear Regulatory Commission Class A LLW grout, and destroy organics and nitrates in the grout feed.
5. No separations—No chemical or radionuclide separations are performed.

Figure 7-3, Waste Separation Technology Options, shows the 11 separations technology options and the no-separations option.

Radionuclide and chemical separations performance summaries for the 11 separations processes and the no-separation option identified above are provided in Tables 7-1 and 7-2, respectively. Summary process descriptions and flow schematics for the 12 separations technology options shown in Figure 7-3 are provided in Section 7.2. Detailed process descriptions, process bases and assumptions, flowsheets containing process flow diagrams and mass balances, generic TRUEX model output, equipment lists, and facility layouts are presented in Appendix G for the two in-tank sludge wash, the four sludge wash, the four TRUEX, Clean, and the no-separation options.

Figure 7-3. Waste Separations Technology Options.

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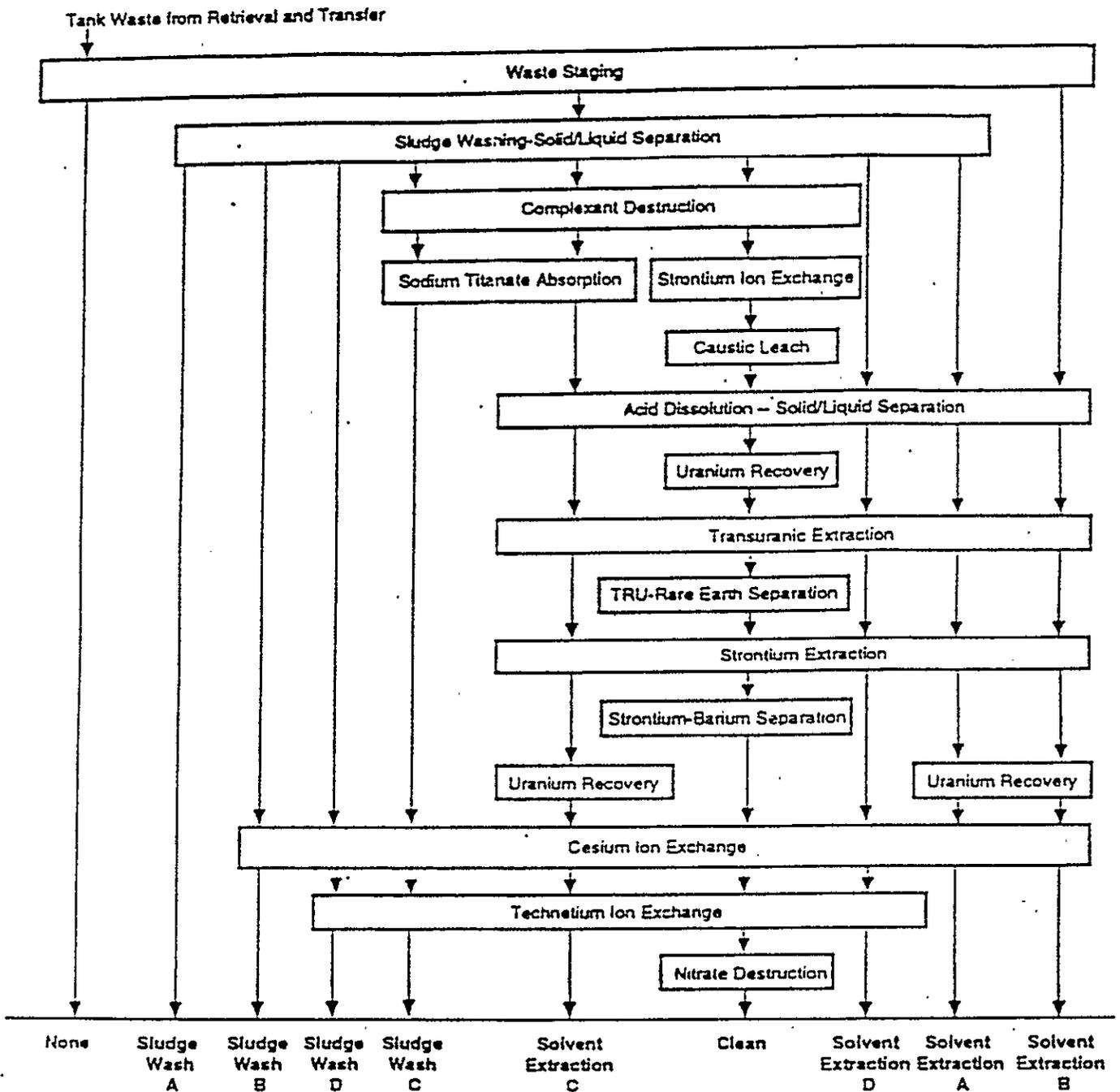


Table 7-1. Radionuclide Separations Summary.

Radionuclide separations to onsite disposal, percent of DST and SST waste inventory												
Separations process option												
Radionuclide	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	No separations, offsite disposal
Americium	5	5	5	5	0.1	5	5	1	1	5	WIP	0
Cesium	89	1	89	1	1	1	1	1	1	1	WIP	0
Plutonium	4	4	3	3	0.1	3	4	1	1	4	WIP	0
Strontium	2	2	1	1	0.1	1	2	1	1	2	WIP	0
Technetium	77	77	77	77	1	1	79	10	1	1	1	0
Uranium	6	6	6	6	0.1	6	6	1	1	86	WIP	0

DST = Double-shell tank

SST = Single-shell tank

WIP = Work in progress

Table 7-2. Chemical Separations Summary.

Chemical separations to onsite disposal, percent of DST and SST inventory												
Separations process option												
Component	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	No separations, offsite disposal
Aluminum	54	54	53	53	37	53	87	87	85	87	WIP	0
Bismuth	25	25	25	25	0	25	76	71	68	76	WIP	0
Calcium	7	7	6	6	0	6	90	91	90	90	WIP	0
Cadmium	21	21	21	21	0	21	86	86	82	86	WIP	0
Cerium	2	2	1	1	0	1	2	1	1	2	WIP	0
Chromium	24	24	24	24	0	24	92	92	90	92	99	0
Iron	2	2	1	1	0	1	105	296	116	101	WIP	0
Manganese	11	11	10	10	10	10	91	91	91	91	WIP	0
Nickel	1	1	0	0	0	0	1	1	1	1	WIP	0
Phosphorus	51	51	51	51	51	51	95	97	95	95	WIP	0
Silicon	3	3	2	2	2	2	10	10	10	10	WIP	0
Sodium ^a	99	102	98	106	111	111	130	326	140	135	WIP	0
Zirconium	3	3	2	2	2	2	92	92	92	92	WIP	0
Nitrite	100	100	99	99	99	99	99	0	99	99	WIP	0
Nitrate ^b	99	100	99	106	102	106	142	468	148	142	5	0
Sulfate	98	98	98	98	98	98	100	100	100	100	WIP	0

^aAdditional sodium and NO₃ added for cesium ion exchange processing.

^bAdditional sodium and NO₃ added for transuranic extraction, strontium extraction, and cesium ion exchange processing.

DST = Double-shell tank

SST = Single-shell tank

WIP = Work in progress

7.1.3 Other Separations Technology Options

Other separations technology options have been identified with potential benefits that are currently under research and have an incomplete basis for full development of the flowsheet and facility requirements in this draft. As the technology is defined, the other separations technology options may be included as evaluated options. The separations technology options with incomplete definition include calcination/dissolution, fractional crystallization, radio frequency (RF) plasma torch/plasma centrifuge, and in-tank separations processes.

7.1.3.1. Calcination/Dissolution. The calcination/dissolution approach involves heating tank waste in excess of 800 °C (1,472 °F) to destroy organic, ferrocyanide, and nitrate/nitrite compounds, and subsequently leaching the residue with water to remove all soluble materials. The solid residues produced during the thermal treatment consist primarily of sodium hydroxide, aluminum compounds, and metal oxides. Because the water leach will dissolve the NaOH, the aqueous treatment is, in reality, a strong caustic dissolution which also dissolves the aluminum as sodium aluminate. An added benefit is derived from the fact that the transuranic elements will remain with the undissolved fraction, which produces a natural HLW/LLW split.

Previous attempts at calcining high sodium material using conventional calciner concepts (i.e., rotary kiln, spray tower, and fluidized bed) have had limited success due to the molten material plugging the reactors. A large scale, plasma arc demonstration successfully calcined 3,000 lbs. of simulated Hanford tank waste continuously without plugging at the Westinghouse Science and Technology Center, in support of the calcination/dissolution project. This demonstrates that large scale, high throughput, calcination of high sodium wastes is possible. However, calcination consumes electrical energy, requires offgas handling of volatile and entrained material, and uses equipment that must withstand high temperatures and corrosive environments.

Initial calcination/dissolution scoping tests using radioactive 101-SY and 110-U tank waste samples confirm that the bulk non-transuranic material is separated from the insoluble transuranic contaminants. The material that dissolved contained < 1 nanocurie transuranic/gram, which is well below the 100 nanocurie transuranic/gram limit.

The degree to which the aluminum compounds can be solubilized depends on the Na-to-Al ratio. If the sodium concentration is low, incomplete conversion of aluminum results. Subsequent water leaching will leave substantial quantities of aluminum in the remaining solids. This effect was noted in the above tests where a large portion of the aluminum did not dissolve. The two tests did not target aluminum dissolution and several alterations to the original test procedure are planned.

Calcination/dissolution may provide a means to further reduce the transuranic volume planned for disposal. The chrome, iron, and nickel in the residue might be reduced to produce a non-TRU metal capable of direct disposal as LLW. The unreduced material would

be subjected to the same aqueous leach as described above. Removal of the transition metals, aluminum, and sodium should reduce subsequent canister count to levels similar to solvent extraction expectations.

7.1.3.2 Fractional Crystallization. Fractional crystallization is used to purify water soluble compounds by controlled growth of solids from a supersaturated solution. Purification occurs by rejection of impurities at the liquid/solid interface. This kind of purification rejects impurities which are incompatible with the growing crystal because of atomic size, charge, or molecular state. Because of this, crystallization rejects almost all contaminants to the liquid phase while producing very pure solid materials.

The crystallization approach presents a new way to reduce radioactivity in grout feed or, in the ultimate, to produce salts sufficiently pure to release from administrative controls. However, crystallization will always leave a residual liquor which is rich in the contaminants rejected during crystal growth. These residual liquors can be treated by conventional means or concentrated further and fed to the HLW waste stream. Much additional work is needed to establish the degree to which crystallization can be used on tank wastes, but a large fraction of the soluble compounds should be considered as being treatable by crystallization.

The fractional crystallization process has limited laboratory data with actual tank waste to develop a flowsheet. A preliminary flowsheet goal developed for treatment of LLW liquid from sludge washing requires a filtered, clear solution for feed and produces about 90 percent of the sodium salts in the waste as nonradioactive purified salt. A salt splitting process is required to separate sodium nitrate into caustic and nitric acid. This commercial splitting process would use part of the recovered salt. About five stages of crystallization and filtration will be required to achieve nonradioactive status. Fractional crystallization has been widely used for commercial purification of nitrate salts. This commercial experience can be used for a projection of approximate equipment requirements, however, no such projection has been done.

7.1.3.3. Radio Frequency Plasma Torch/Plasma Centrifuge. The RF Plasma Torch/Plasma Centrifuge (PT/C) process is a newly emerging system currently under development for material dissociation and mass separation application on complex feed streams. The PT/C system consists of two main components: an RF-induced plasma torch disassociator and an electro-magnetic (E cross B) plasma centrifuge. The RF torch uses inert gas ionized by RF inductive heating to create a plasma dissociation zone with electron energies in the 1-10 eV range. This plasma zone is of sufficient size and temperature to dissociate compounds in the feed stream into their constituent elements, with partial ionization of these elements). The product from the RF torch flows into the plasma centrifuge, where an electro-magnetic torque causes the partially ionized plasma stream to rotate at high tangential velocities. Collisions of the rotating plasma with the un-ionized elements induces all of the material within the centrifuge to rotate: thus enabling heavy mass particles to be separated from lighter mass particles.

Although RF induced plasmas have been used for a variety of small-scale, low-pressure research applications: the ability to produce large-scale, high-pressure RF plasmas has only recently been achieved. The use of plasma centrifuges for mass separation has also been studied, primarily for isotope separation at low pressures. Merging of these two plasma method into a PT/C system is a new concept that offers a number of advantages over other separation techniques. Firstly, this system does not require any chemical preprocessing of feed material provided the particle size is small enough. Secondly, only partial ionization of the material stream is needed to obtain high spin velocities; and thus the neutral reactant elements are not too greatly heated. Thirdly, this technology is based completely upon the electro-magnetic manipulation of the materials: and thus has no moving parts. Moreover, the RF torch antenna are outside of the plasma zone container, and thus are not exposed to the waste stream unlike the electrodes in some dc arc torch systems).

Preliminary calculations have been performed for a PT/C system application to the Hanford Site single-shell tank (SST) waste stream (of approximately 200,000 Mg, including added water), by assuming that a PT/C system would be capable of complete dissociation of the input feed and a 99 percent separation efficiency of all elements above 80 atomic mass units (amu). These calculations indicate that such a process would result in approximately 6,000 canisters of HLW. Because of a relatively large mass differential between waste stream elements, a high separation efficiency is possible within a single stage. However, a number of different phenomena may have a tendency to reduce this separation efficiency. One such phenomenon is related to the interaction of particles within the centrifuge. Particle collisions and momentum transfer, which induces the spinning within the centrifuge, may result in the recombination of lighter elements into particles having effective masses greater than 80 amu. These particles will be separated along with the heavier elements, thus reducing the overall separation efficiency. The centrifuge design will most likely be one which balances an optimal separation efficiency against a reasonable throughput. Additional research and development is necessary to predict accurately the number of separation stages which will be required to process all of the tank waste.

Estimates of PT/C unit size and throughput are as follows: A 1 MW (megawatt) PT/C unit would be approximately 1.5 m (5 ft) in diameter and 9 m (30 ft) long. (These are rough dimensions of a basic unit, not including the necessary external power supplies, vacuum system pumps, and cooling system pumps.) Such a device may be capable of processing approximately 500 kg of waste per hour. At this rate, 20 units operating at 50 percent availability would be able to process all of the SST and DST waste (assuming 345,000 Mg total waste) in 7-8 years. The method of collection for both the light and heavy streams still need to be developed. One proposed method for collecting the HLW stream is the use of removable cylindrical liners located on the inside walls of the centrifuge. Depending on the amount of material collected, these liners may require replacement at intervals of 1/day to 1/week.

The separation plant will probably be a large canyon type facility utilizing numerous process cells for remote PT/C operation and maintenance, remote heavy stream product handling, remote light stream product handling, and associated remote solid and liquid

effluent handling. This facility will require the support of other Hanford Site waste handling operations. Integration of this facility with Hanford Site waste handling operations is shown in Figure 7-4.

7.1.3.4 In-Tank Separations Processing.

The performance of the onsite disposal waste form can be improved by removing TRU, ^{90}Sr and ^{99}Tc from alkaline waste solutions. The concentrations of TRU and ^{90}Sr are high in some alkaline wastes because these radionuclides exist as soluble complexes with organic chelating agents. Technetium is present as the soluble TcO_4^- anion. Methods for removing these radionuclides from alkaline Hanford waste solutions are not well developed; however, initial scouting tests are underway. Further testing is warranted because of the possibility that simple carrier precipitation or scavenging methods could potentially be performed in-tank. Appendix B discusses technology development requirements for these processes. Following are brief descriptions of candidate methods that should be evaluated.

Hydroxide Adjustment for Precipitation of TRU and ^{90}Sr —Ryan (1992) reviewed tank waste sample characterization data that suggest possible TRU element precipitation from complexed wastes with increasing free hydroxide concentrations. Addition of hydroxide will likely also reduce ^{90}Sr solubility. Laboratory tests should include addition of scavenging agents such as Fe^{3+} to promote rapid precipitation.

Sulfide Precipitation of ^{99}Tc —Small concentrations of sulfide have been shown to precipitate Tc(VII) as Tc_2S_7 which is extremely insoluble (O'Kelley 1987). Technetium is also strongly sorbed by antimony sulfide, and Fe^{2+} bearing sulfide minerals (Bock et al., 1989), thus promoting consideration of sulfidic compounds for repository backfill minerals. Tests need to be performed with actual waste solutions to assess precipitation methods and the use of preformed scavengers (e.g., sulfide minerals) for removing ^{99}Tc from alkaline wastes.

Strontium Isotopic Swamping—Alkaline wastes containing soluble sulfates or phosphates will upon addition of inert $\text{Sr}(\text{NO}_3)_2$, form insoluble $\text{Sr}_3(\text{PO}_4)_2$ or SrSO_4 precipitates. Formation of these precipitates will likely result in isotopic exchange and co-precipitation of ^{90}Sr held in solution as soluble complexes with organic chelating agents. This isotopic swamping or dilution technique in conjunction with addition of hydroxide (described earlier) could significantly reduce the ^{90}Sr content in complexed wastes.

Selective Removal of Certain Non-Radioactive Components—Many of the solid fractions of DST and SST wastes contain large amounts of aluminum and phosphorous that limit glass waste loadings and result in large numbers of HLW glass canisters. Known chemistry suggests that leaching of tank sludges with a warm NaOH solution would dissolve hydrated aluminum oxide and metathesize phosphate precipitates to hydroxide precipitates and soluble Na_3PO_4 . This process is being performed at the Savannah River Site (SRS) to reduce the volume of feed to the glass melter at the Defense Waste Processing Facility.

Figure 7-4. Radio Frequency Plasma Centrifuge Flow Schematic.

FIGURE NOT AVAILABLE

However, for aged Hanford wastes, much of the aluminum may be present as gibbsite or bauxite, aluminum hydroxide minerals that are relatively insoluble in alkaline solutions.

None of the above candidate processes have been demonstrated with Hanford Site wastes to an extent that process flowsheet conditions, process throughput rates, or separation efficiencies can be defined. Thus, these processes are not evaluated in this report as candidate waste separation technologies. The In-Tank Sludge Wash processes defined in this report will be modified as laboratory data become available.

G1.1 SELECTION OF SEPARATIONS TECHNOLOGY OPTIONS

This section describes the selection of separations technology options for evaluation. The separations technology options discussed in this appendix are made up by combining individual unit processes to attain the overall process desired. The individual unit processes were initially identified by literature reviews of radionuclide separations processes. Unit processes were then selected from the identified processes based on technology demonstration status.

G1.1.1 Identification of Unit Separations Processes

Unit radionuclide separations processes are shown in Figure G1-1, Separation Technology Options. Unit processes used in the separations technology options are identified by the heavy lines and are discussed in Sections G1.1.1.2 and G1.1.1.3. Unit processes not used in separations technology options are identified with light lines and a note explaining the reason for rejection. More detailed discussions of the rejected technologies with references are provided in Section G1.1.3.

The organization of Figure G1-1 follows treatment of tank wastes with pyrochemical, aqueous acidic, or aqueous alkaline processes. Following are the criteria for selection or rejection of the aqueous processes shown in Figure G1-1.

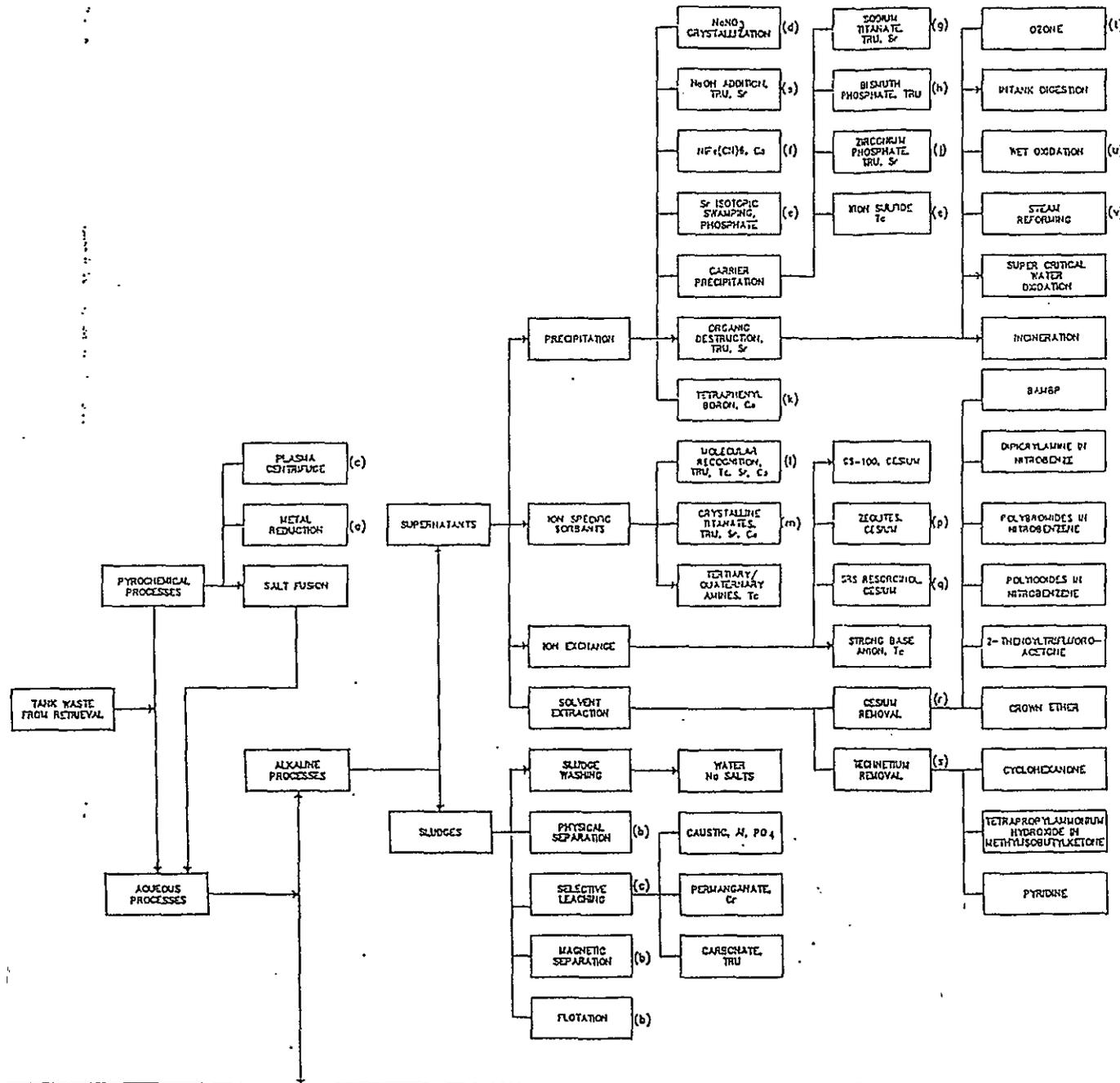
G1.1.1.1 General Criteria. For plant-scale nuclear applications, continuous countercurrent liquid-liquid solvent extraction processes, when available, are generally preferred over ion exchange, precipitation or extraction chromatographic processes. Over 40 years of successful experience in the United States and elsewhere demonstrate that liquid-liquid solvent extraction processes can be operated on a large scale to accomplish, routinely and satisfactorily, high throughput nuclear separations in well-established and readily available contacting equipment.

In those cases where solvent extraction technology is either not available or, for some reason, not desirable, fixed-bed ion exchange processes are usually preferred over either precipitation or extraction chromatographic processes. Fixed-bed load-wash-elute ion exchange processes were successfully used on a plant-scale at the Hanford Site to separate

SEPARATION TECHNOLOGY OPTIONS - SHEET 1

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Figure G1-1. Separation Technology Options. (sheet 1 of 2)



LEGEND

PROCESSES NOT EVALUATED

EVALUATED PROCESSES

NOTES

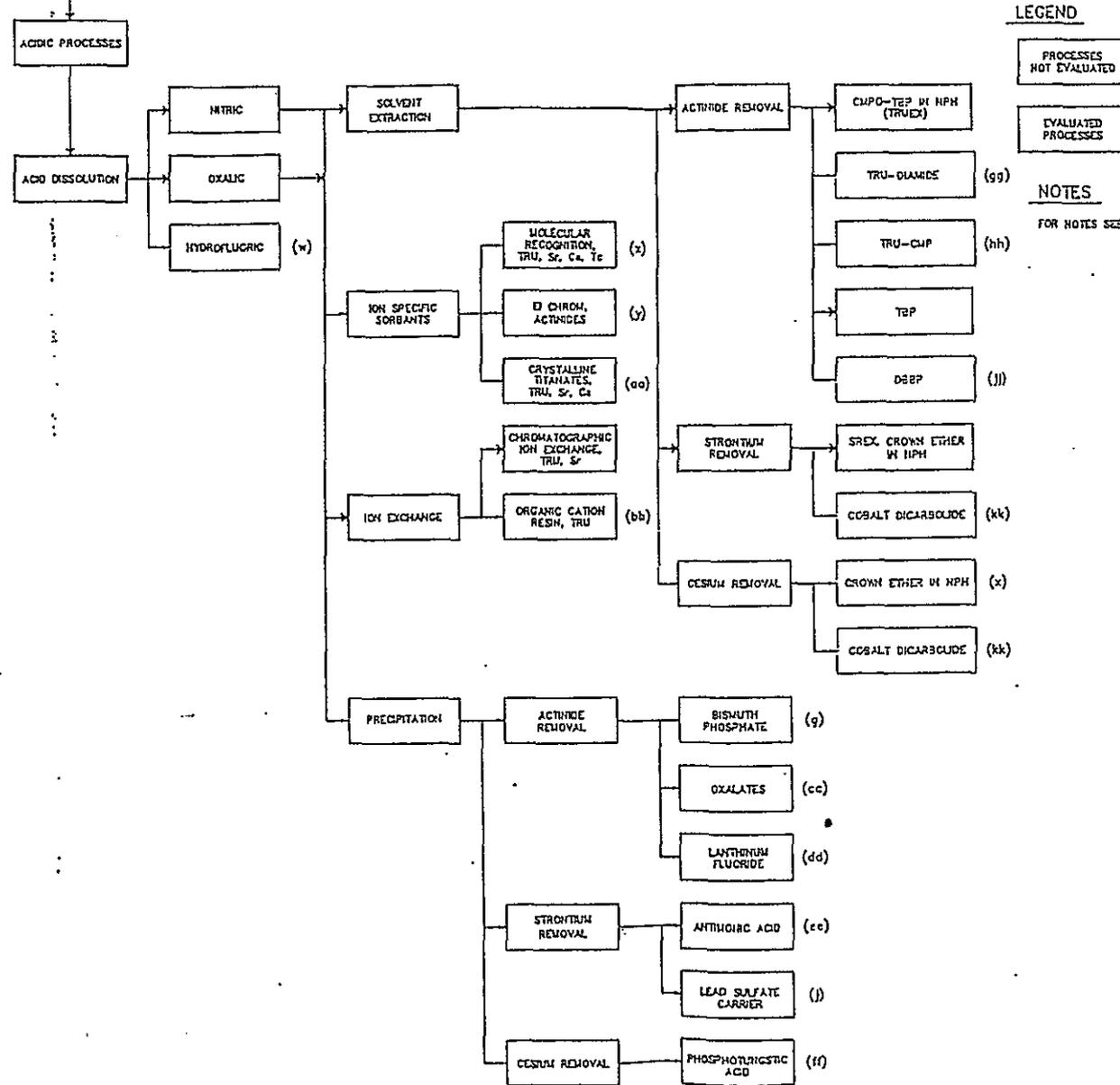
- (a). APPLICABILITY IS UNCERTAIN--STAGED DEVELOPMENT.
- (b). UNTESTED FOR REMOVING SELECTED SLUDGE COMPONENTS.
- (c). LIMITED LABORATORY TESTS--APPLICABILITY IS UNSURE.
- (d). A CONCENTRATION METHOD, NOT REMOVAL.
- (e). RELATIVELY UNTESTED FOR HANFORD ALKALINE SUPERNATANTS.
- (f). MUST CAREFULLY CONTROL pH; FERROCYANIDE IS SAFETY ISSUE.
- (g). LIKELY NOT EFFECTIVE FOR COMPLEXED Sr AND TRU; MUST DESTROY COMPLEXANTS FIRST.
- (h). GENERATES EXCESS WASTE, INCREASING CANNISTERS AND VOLUME.
- (i). GENERATES EXCESS WASTE, MAKES GELATINOUS PRECIPITATES.
- (j). HAZARDOUS CHEMICAL; BYPRODUCT MUST BE DESTROYED.
- (k). LIKELY APPLICABLE FOR Cs AND Tc BUT ION-EXCHANGE MORE THOROUGHLY TESTED; COMPLEXANTS MAY INTERFERE WITH Sr AND TRU.
- (l). COMPETITIVE WITH ION-EXCHANGE FOR Cs BUT WOULD ADD HLW VOLUME; COMPLEXANTS MAY INTERFERE WITH Sr AND TRU.
- (m). ZEOLITE CHEMICALLY UNSTABLE; INCREASE GLASS VOLUME.
- (n). COULD REPLACE Cs-137; WOULD NOT CHANGE FLOWSHEET SIGNIFICANTLY.
- (o). PHASE SEPARATION DIFFICULTIES AND TOXIC SOLVENTS.
- (p). RELATIVELY UNTESTED, MUST USE HAZARDOUS DILUENT; EMULSIONS A PROBLEM; WITH ALKALINE SODIUM SOLVENT EXTRACTION PROCESSES.
- (q). COMPLEXANTS NOT COMPLETELY DESTROYED, REQUIRES SIGNIFICANT VOLUMES OF OZONE; PROCESSING IN-TANK PROBABLY NOT PRACTICAL.
- (r). MAY BE COMPETITIVE WITH SODIUM; FURTHER TESTING NEEDED.
- (s). MAY BE BOD AGGLOMERATION WITH HIGH SODIUM WASTE.
- (t). EXCESSIVE SLUDGE VOLATILITY MAY PLUG OFF GAS TRAIN.
- (u). MINIMAL TESTING--POSSIBLE FUTURE PAYOFF.
- (v). TESTING NEEDED--DESIGNED FOR ANALYTICAL PURPOSES.
- (w). REQUIRES ADJUSTMENT TO SLIGHTLY ACID pH.
- (x). INTERFERENCE WITH Fe AND OTHER CATIONS; ANIONIC RESIN ALSO NEEDED FOR Pu AND Np.
- (y). MULTIPLE STEPS NEEDED TO REDUCE CONCENTRATIONS OF ALL TRU ELEMENTS TO < 100 nCi/g IN ACIDIFIED WASTES.
- (z). CLUMBERSOME BATCH PROCESS; INCREASES GLASS COLUMN.
- (aa). DIFFICULT TO RECOVER PRECIPITATE, LOW RECOVERY.
- (ab). REQUIRES RELATIVELY HIGH Cs CONCENTRATION, THUS REQUIRES ISOTOPIC DILUTION; INCREASE IN CANNISTERS.
- (ac). EXHIBITS HYDROLYTIC DEGRADATION; POOR DECONTAMINATION FROM Fe.
- (ad). LIMITED TESTING COMPARED TO TRUCK PROCESS. FURTHER TESTING REQUIRED.
- (ae). DIFFICULT TO ADEQUATELY EXTRACT ALL ACTINIDES AT SINGLE ACIDITY.
- (af). HAZARDOUS DILUENT--NOT TESTED IN US.

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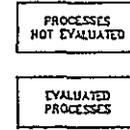
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SEPARATION TECHNOLOGY OPTIONS - SHEET 2

Figure G1-1. Separation Technology Options. (sheet 2 of 2)



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NOTES

FOR NOTES SEE DRAWING ALB138

megacurie amounts of ^{137}Cs . Precipitation processes also have been used at the Hanford Site for separation of plutonium, ^{137}Cs , ^{90}Sr , and fission product rare earths.

Precipitation processes are batch rather than continuous processes; simple batch precipitation processes typically are incapable of removing >99 percent of a particular radionuclide or group of radionuclide and also do not provide acceptable decontamination of separated radionuclides from contaminants. Extraction chromatographic processes are useful for small volume highly specialized separations, e.g., trivalent actinides from trivalent rare earths, but because of capacity and selectivity limitations, are not particularly useful for handling large volumes of feed.

G1.1.1.2 Separation of Radionuclides from Acidic Wastes.

TRU Elements and Technetium-99--For reasons already stated, liquid-liquid extraction processes are preferred over precipitation (e.g., oxalates or fluoride) processes or extraction chromatographic processes for separation of TRU elements from acidified wastes. Bifunctional extractants, e.g., carbamoylmethylenephosphine oxides (CMPO), are much preferred over monofunctional reagents such as dibutylbutylphosphonate because they efficiently extract Am^{+3} as well as +4 and +6 actinides from strongly acidic, i.e., >0.5M HNO_3 feeds. For several reasons, e.g., commercial availability, ability to co-extract ^{99}Tc , decontamination potential, etc., one particular CMPO, namely octylphenyl-N,N-diisobutylcarbamoylmethylenephosphine oxide, is the currently preferred TRU element extractant.

Strontium-90--Processes that effectively and selectively remove ^{90}Sr from strongly acidic solutions are difficult to devise. The currently best available technology appears to be the strontium extraction (SREX) process, a solvent extraction process employing as the extractant a commercially available crown ether diluted with n-octanol or tributyl phosphate (TBP) and normal paraffin hydrocarbon (NPH). The SREX process is highly selective for Sr^{+2} over a wide range of feed acidities; only Ba^{+2} co-extracts to any extent. Dilute HNO_3 solutions readily strip Sr^{+2} from the solvent.

Two other processes are potentially available for separating ^{90}Sr from acidic media. One of these is the dicarbolyde solvent extraction process long studied by both Russian and Czechoslovakian scientists. According to these investigations, dicarbolydes effectively and selectively extract both Cs^+ and Sr^{+2} from acidic media provided a polyglycol is added to the feed. A major, perhaps insurmountable, disadvantage of the dicarbolyde extraction process is that the required diluents are nitrobenzene or chlorinated benzenes. Such toxic diluents are no longer acceptable for use in U.S. nuclear separation plants.

Crystalline polyantimonic acid also effectively and selectively sorbs ^{90}Sr from nuclear acidic wastes. The principal disadvantage to this ion exchanger is that no single and inexpensive way of eluting sorbed ^{90}Sr is known. There are also concerns about the commercial availability of plant-scale quantities of crystalline polyantimonic acid.

Cesium-137—A need to remove ^{137}Cs from acidic waste solutions has not been established. If such removal is required from some acidic solutions, the simplest procedure is to adjust the acid waste to pH 9-10, after prior removal of TRU elements and ^{90}Sr , and use well-known ion exchange materials and procedures for removal of ^{137}Cs .

Subject to the limitations discussed earlier a batch precipitation of cesium phosphotungstate (PTA) could be used to remove about 95 percent of the ^{137}Cs directly from the acid waste. Alternatively, it may be feasible to remove ^{137}Cs from the acid waste by means of the cesium-strontium extraction process. The latter is a solvent extraction process currently just under development at the Argonne National Laboratory; the extractant is a commercially available crown ether. Crystalline sodium titanate has also been reported to sorb ^{137}Cs from acidic media. Applicability of this solvent to Hanford Site acid wastes needs to be determined.

G1.1.1.3 Separation of Radionuclides from Alkaline Wastes.

Technetium-99—The classic and preferred way of removing ^{99}Tc from alkaline waste solutions is to selectively sorb it, as TcO_4^- , on a strong-base organic ion exchanger. Sorbed ^{99}Tc can be eluted with 6M HNO_3 solution.

Various organic compounds, e.g., cyclohexanone, pyridine, tetrapropylammonium hydroxide, are known to extract ^{99}Tc from alkaline wastes. Of these reagents, cyclohexanone appears most promising and has been studied on a bench-scale with actual Hanford Site wastes. Further work including pilot-plant scale tests with the cyclohexanone extraction process are required to determine the extent of emulsion problems in solvent extraction of the alkaline waste solution.

Cesium-137—Organic cation exchange resins were employed very successfully at the Hanford Site on a plant-scale for many years to remove ^{137}Cs from alkaline wastes. Such technology using newer resins, e.g., Duolite CS-100¹ or a resorcinol-based exchanger developed at the Savannah River Site is still the preferred technology for removing ^{137}Cs from alkaline tank wastes.

Alternative methods for removing ^{137}Cs from alkaline solutions all appear to have disadvantages compared to well-established ion exchange technology. Thus, various precipitation agents; e.g., tetraphenyl boron, nickel ferrocyanide, etc., must all be applied on a batch basis and, in a single precipitation step, may not give required yields. Furthermore, downstream treatment of the cesium-laden precipitates involves potential safety hazards. Candidate solvent extraction processes employing such extraction as BAMBIP, dipicrylamine, polybromides, and crown ethers have not either been fully developed or require use of toxic diluents such as nitrobenzene.

¹Duolite CS-100 is a registered trademark of Rohm and Haas, Philadelphia, Pennsylvania.

Destruction of Organic Complexants--Leading candidates for organic destruction include heat and digest, supercritical water oxidation (SCWO), and incineration. In-tank digestion will degrade components that result in hydrogen generation; (e.g., ethylenediaminetriacetic acid [HEDTA]). Incineration and SCWO will degrade organic materials to $\text{CO}_2 + \text{H}_2\text{O}$, and will also result in precipitation of ^{90}Sr and TRU elements. Other candidates, including wet oxidation and steam reforming, may be competitive with SCWO but need further development.

G1.1.2 Combination of Unit Processes Into Technology Options

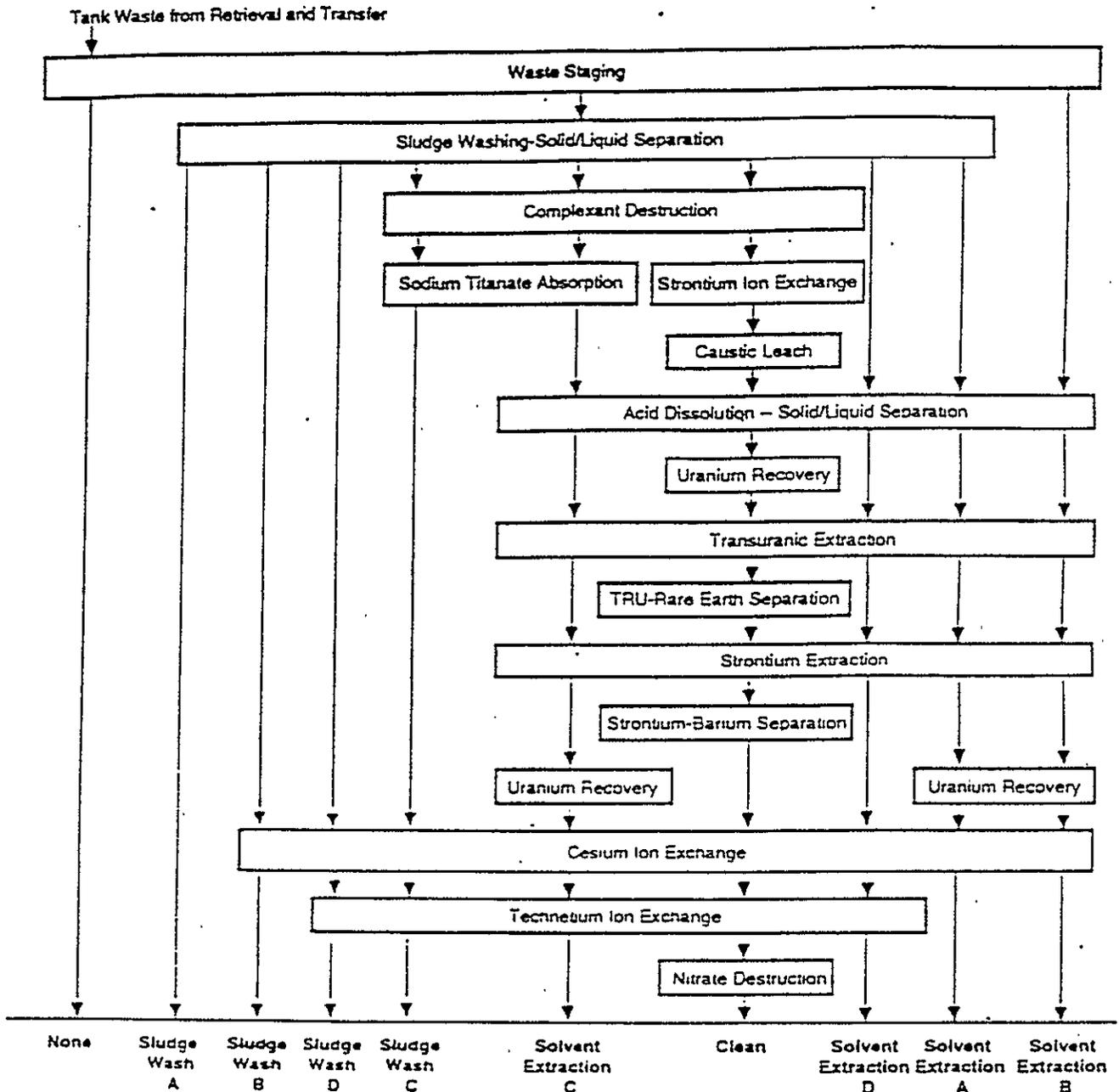
The unit processes selected on the basis of technology status are combined into five basic processing options with different levels of separations performance.

1. **In-Tank Sludge Washing**--Transfer waste to double-shell tanks (DST) where supernatant is decanted and sent to onsite disposal. Wash the remaining solids and then decant the soluble components to onsite disposal. Treat the washed solids for offsite disposal. Two levels (A and B) of radionuclide removal are defined.
2. **Sludge Washing**--Separate solids or sludges from supernatant and wash solids with dilute caustic to remove soluble salts. Treat the insoluble solids for offsite disposal. Four levels (A, B, C, and D) of radionuclide removal are defined.
3. **Solvent Extraction (transuranic extraction and strontium extraction) Processing**--Separate solid and liquid (sludge washing) and further reduce waste solids requiring HLW treatment by acid dissolution of the sludges. The transuranic extraction process results in an approximate factor of 3 reduction in volume of glass for offsite disposal. TRU components are removed from the acidic waste for treatment and offsite disposal. Four methods or levels (A, B, C, and D) of supplemental radionuclide removal are defined.
4. **Clean**--Separate solid and liquid fractions and further reduce waste solids requiring HLW treatment by (a) caustic and multiple acid leaches of the sludges, (b) extraction of radionuclides from aqueous solutions, and (c) separate inert elements from recovered radionuclide fractions. The goal of the Clean process is to reduce HLW to less than 1,000 canisters, produce a U.S. Nuclear Regulatory Commission class A LLW grout, and destroy organic materials and nitrates in the grout feed.
5. **No Separations**--No chemical or radionuclide separations are performed.

Figure G1-2, Waste Separations Options, shows the 11 separations technology options and the no-separations option.

Figure G1-2. Waste Separation Options.

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Radionuclide and chemical separations performance summaries for the 11 separations processes and the no-separation option identified above are provided in Tables 7-1 and 7-2, respectively. Summary process descriptions and flow schematics for the 12 separations technology options shown in Figure 7-3 are provided in Section 7.2. Detailed process descriptions, process bases and assumptions, flowsheets containing process flow diagrams and mass balances, generic TRUEX model output, equipment lists, and facility layouts are presented in Sections G2.0 through G13.0 for the two in-tank sludge wash, the four sludge wash, the four solvent extraction, Clean, and the no-separation options.

G1.1.3 Separations Processes Not Selected for Evaluation

The following are separations processes that were not evaluated for the *Tank Waste Technology Options Report*. Sheet 1 of Figure G1-1 lists alkaline separations processes (a through v) and sheet 2 lists acid side processes (w through kk).

a. Radio Frequency Plasma Torch/Plasma Centrifuge

The Radio Frequency (RF) Plasma Torch/Plasma Centrifuge (PT/C) process is a newly emerging system currently under development for material dissociation and mass separation application on complex feed streams. The PT/C system consists of two main components: an RF-induced plasma torch dissociator and an electromagnetic (E cross B) plasma centrifuge. The RF torch uses inert gas ionized by RF inductive heating to create a plasma dissociation zone with electron energies in the 1-10 eV range. This plasma zone is of sufficient size and temperature to dissociate compounds in the feed stream into their constituent elements, with partial ionization of these elements. The product from the RF torch flows into the plasma centrifuge, where an electromagnetic torque causes the partially ionized plasma stream to rotate at high tangential velocities. Collisions of the rotating plasma with the unionized elements induces all of the material within the centrifuge to rotate, thus enabling heavy mass particles to be separated from lighter mass particles.

The RF PT/C process has an incomplete basis for full development of the flowsheet and facility requirements in this draft. As the technology is defined, it may be included as an evaluated option. Additional discussion of the RF PT/C process is provided in Chapter 7.0, Section 7.1.3.3.

b. Physical Separation

The separation of radionuclides from inert elements by physical separation is based on particle size or magnetic properties of the solid particles and compositional differences between particles. There is an incomplete definition of composition and physical properties of sludge particles for the different waste types to serve as a basis for development of flowsheets and facility requirements. As the technology is defined, it may be included as an evaluated option.

c. Selective Leaching Processes

Several processes have been identified that could be performed on waste sludges to potentially reduce the volume of the waste requiring treatment for offsite disposal. These processes represent an intermediate position between simple water washing of sludges, and dissolution of the sludges in acid followed by removal of radionuclides from the dissolved sludge solutions. None of the candidate processes have been demonstrated with Hanford Site wastes to an extent such that process flowsheet conditions, process throughput rates, or separations efficiencies can be defined. Thus, these processes are not evaluated in this report as candidate waste separations technologies. Laboratory tests to evaluate the application of these processes are warranted (see Appendix B). The following are brief descriptions of promising selective leaching processes.

- **Selective removal of certain nonradioactive components.** Many of the solid fractions of DST and single-shell tanks (SST) wastes contain a large amount of certain nonradioactive components that limit glass waste loadings. For example: Plutonium Finishing Plant (PFP) waste and CC waste solids contain significant amounts of chromium and aluminum while the solid portion of neutralized cladding removal waste (NCRW) essentially is hydrated zirconium oxide.

Some preliminary bench-scale tests with actual PFP waste solids indicate that washing with dilute potassium permanganate (KMnO_4) solution oxidizes insoluble chromium (III) to soluble chromium (VI). Also, water washing of PFP waste solids removes part of the phosphorus content. One bench-scale test with actual NCRW solids indicates that oxalic acid may remove some of the zirconium. Known chemistry suggests that leaching of PFP waste, CC waste solids, and possibly some SST wastes with a warm NaOH solution would dissolve hydrated aluminum oxide. This process is being performed at Savannah River Site (SRS) to reduce the volume of feed to the glass melter at the Defense Waste Processing Facility. However, for aged Hanford Site wastes, much of the aluminum may be present as gibbsite or boehmite, aluminum hydroxide minerals that are relatively insoluble in alkaline solutions.

- **Selective Leaching of Transuranic Elements.** Special aqueous solutions can potentially selectively leach TRU elements from waste solids. The leached solids could possibly be disposed of as LLW. Laboratory-scale tests with actual NCRW solids indicate that it may be possible to leach the TRU elements without dissolving much of the inert components. Promising TRU removal procedures and reagents include dilute HNO_3 -silver persulfate solutions, sodium carbonate-sodium bicarbonate solutions containing an oxidant such as potassium ferrate, and catalyzed electrolytic plutonium oxide dissolution (CEPOD) technology.

d. Sodium Nitrate Crystallization

The NaNO_3 crystallization process is intended for application to aqueous solutions of salt cake in SSTs and, perhaps, to aqueous waste solutions in DSTs. The goal of the NaNO_3 crystallization process is to partition acidified aqueous waste solutions into a small volume of aqueous solution containing TRU elements, ^{90}Sr , ^{99}Tc , ^{137}Cs , (and perhaps, other radionuclides) and a much larger volume of solid NaNO_3 containing only small concentrations of radionuclides. To achieve such partitioning, alkaline waste solutions will be adjusted to a pH in the range 1 to 2, thermally concentrated to exceed the solubility of NaNO_3 , and cooled. Crystallized NaNO_3 is separated (e.g., by filtration), washed with a saturated solution of NaNO_3 , and dissolved in water. The resulting solution is again adjusted to a pH in the range 1 to 2, and NaNO_3 crystallized a second time and washed again. The combined supernatant and spent washes containing concentrated radionuclides constitutes feed for downstream radionuclide separations operations.

Bench-scale development of the NaNO_3 crystallization process is just underway. Currently perceived technical issues that could prevent its large-scale implementation include (1) the need for many crystallization stages to achieve adequately decontaminated (e.g., U.S. Nuclear Regulatory Commission class A waste) NaNO_3 , and (2) the need to separate (e.g., filter) large masses of solid NaNO_3 after each crystallization stage.

e. Precipitation Methods for Removal of Transuranic, ^{90}Sr , and ^{99}Tc From Alkaline Wastes

The performance of the LLW disposal form can be improved by removing TRU, ^{90}Sr , and ^{99}Tc from alkaline waste feed solutions. The concentrations of TRU and ^{90}Sr are high in some alkaline wastes because these radionuclides exist as soluble complexes with organic chelating agents. Technetium is present as the soluble TcO_4^- anion. Methods for removing these radionuclides from alkaline Hanford Site waste solutions are not well developed; however, initial scouting tests are underway. Further testing is warranted because of the possibility that simple carrier precipitation or scavenging methods could potentially be performed in-tank. Chapter 7.0 and Appendix B discuss technology development requirements for these processes.

Following are brief descriptions of candidate methods that should be evaluated.

- Hydroxide adjustment for precipitation of TRU and ^{90}Sr . Ryan (1992) reviewed tank waste sample characterization data that suggest possible TRU element precipitation from complexed wastes with increasing free hydroxide concentrations. Addition of hydroxide will likely also reduce ^{90}Sr solubility. Laboratory tests should include addition of scavenging agents such as Fe^{+3} to promote rapid precipitation.
- Sulfide precipitation of ^{99}Tc . Small concentrations of sulfide have been shown to precipitate Tc(VII) as Tc_2S_7 ; this is extremely insoluble (O'Kelley 1987).

Technetium is also strongly sorbed by antimony sulfide, and Fe^{+2} bearing sulfide minerals (Bock et al. 1989), thus promoting consideration of sulfidic compounds for repository backfill minerals. Tests need to be performed with actual waste solutions to assess precipitation methods and the use of preformed scavengers (e.g., sulfide minerals) for removing ^{99}Tc from alkaline wastes.

- Strontium Isotopic Swamping. Alkaline wastes containing soluble sulfates or phosphates will form, upon addition of inert $\text{Sr}(\text{NO}_3)_2$, insoluble $\text{Sr}_3(\text{PO}_4)_2$, or SrSO_4 precipitates. Formation of these precipitates will likely result in co-precipitation of ^{90}Sr . This isotopic swamping technique in conjunction with addition of hydroxide (described earlier) could significantly reduce the ^{90}Sr content in highly complexed wastes.

f. Nickel Ferrocyanide Precipitation of ^{137}Cs

In the 1950's, investigators at the Hanford Site examined many different metal ferrocyanide compounds to co-precipitate (or scavenge) ^{137}Cs from aged, alkaline nitrate waste solutions. Highly successful results were obtained by precipitation of $\text{Cs}_2\text{Ni}[\text{Fe}(\text{CN})_6]$; in the middle 1950's, large-scale removal of ^{137}Cs from aged BiPO_4 process alkaline wastes was performed by precipitation of this compound. Later, workers adapted the nickel ferrocyanide precipitation process to efficient removal and recovery of ^{137}Cs from freshly-produced Hanford Site PUREX Plant HLW (Schulz and Bray 1987).

The presence of nickel ferrocyanide precipitates in waste sludges stored in SSTs has recently been identified as a potential safety issue. Under certain conditions (i.e., elevated temperatures and dry conditions), nickel ferrocyanide has been demonstrated to decompose explosively. Although these conditions are not considered attainable in Hanford Site tanks, the nickel ferrocyanide precipitation process was not considered in this *Tank Waste Technical Options Report* because of the potential safety ramifications. Rather, removal of ^{137}Cs from alkaline solutions was evaluated using well known cation exchange methods that have been demonstrated at both the Hanford Site and SRS.

g. Sodium Titanate Precipitation from Alkaline Solutions

Removal of trace amounts of ^{90}Sr and TRU elements from alkaline waste solutions by co-precipitation with sodium titanate has been demonstrated in the SRS laboratories. In-tank precipitation of ^{90}Sr and TRU elements from Hanford Site alkaline waste (such as CC waste) using hydrous sodium titanate would be a convenient method of preparing the supernatants for feed to a LLW solidification process (e.g., grout) for onsite disposal. The solubility of ^{90}Sr and TRU is quite high in Hanford Site CC waste because of the presence of organic complexing agents. Work by Schulz (1980) showed that ^{90}Sr was not removed from actual complexed waste that was passed through a column containing sodium titanate. These results tend to indicate that sodium titanate may not remove other complexed species such as ^{239}Pu . No other tests with actual CC wastes are believed to have been performed to date. Because of the lack of clear evidence that ^{90}Sr and TRU elements can successfully be removed by

sodium titanate from alkaline waste solutions containing organic complexants, this process was included in the *Tank Waste Technical Options Report* only for processes that destroyed the organic complexants before removal of the ^{137}Cs .

h. BiPO_4 Precipitation of Transuranic Elements

The BiPO_4 precipitation process was the first nuclear separations process ever used on a large scale in the U.S. and, indeed, in the world. Performed in acidic medium, e.g., 0.5 to 1.0M HNO_3 , precipitation of BiPO_4 efficiently coprecipitates +4 Pu and Np. The BiPO_4 process has never been applied in highly alkaline media. It is not even known if Bi^{+3} will precipitate as BiPO_4 in such a solution. Under these conditions, trivalent bismuth may selectively precipitate as hydrated bismuth trioxide. In any event, BiPO_4 even when precipitated from acidic solutions does not coprecipitate Am^{+3} .

j. Zirconium Phosphate

Addition of a soluble Zr(IV) salt to phosphoric acid solutions results in the precipitation of a gelatinous amorphous solid of variable composition and properties. Crystalline compounds can be prepared by refluxing such gels in strong phosphoric acid. Clearfield (1982) has prepared an excellent summary of the properties of various types of amorphous and crystalline zirconium phosphates.

From time to time, various researchers have suggested use of solid pre-formed zirconium phosphate materials for sorbing Pu(IV) from weakly acidic media, generally for analytical-scale applications. But, no serious consideration of plant-scale use of zirconium phosphate for sorption of actinides from either alkaline or acidic waste solutions has been reported. Not only are there more convenient and efficient ways to accomplish such hydrodynamic separations, but zirconium phosphate solids do not lend themselves to conventional column use; they also exhibit poor hydrodynamic properties and tend to bleed phosphorous in alkaline solutions. Under some conditions in alkaline media, zirconium phosphate is unstable with respect to formation of gels.

k. Removal of ^{137}Cs Using Tetraphenyl Boron

Sodium tetraphenyl boron (TPB) precipitation of ^{137}Cs from alkaline solutions is the reference process to be used at the SRS. The reacted ^{137}Cs -TPB forms a flocculent precipitate that floats on the surface and will require physical separation. At SRS, acid hydrolysis of the ^{137}Cs -TPB will be performed to recover the hazardous benzene, followed by incineration to mitigate the release of benzene. Although the DF's for ^{137}Cs are very high with TPB, large masses of chemicals are needed to achieve the required DF's. Because of the need for using large masses of chemicals and the requirement of treating the benzene byproduct, alkaline cation exchange processes that have been used extensively at the Hanford Site were evaluated in the systems engineering study for removing ^{137}Cs from alkaline supernatants.

l. Molecular Recognition Process for Removal of Transuranic, Technetium, Strontium, and Cesium

Molecular recognition is a separation process that combines the selectivity of solvent extraction with the multistage attributes of fixed bed chromatographic systems. The extractant, a macrocyclic crown ether, is impregnated on a solid substrate. The waste solution is passed through the bed where the specific radionuclide of interest is sorbed. Different crown ether reagents can be used to selectively remove cesium, strontium, technetium, or TRU elements. Advantages sometimes claimed for fixed bed sorption processes over liquid-liquid extraction systems include the use of simple process equipment and lower capital costs for process equipment. However, very little testing of the application of molecular recognition separations with either synthetic or actual Hanford Site alkaline wastes has been performed. Further testing is warranted.

m. Crystalline Titanates

Use of crystalline titanates (sometimes called silico-titanates) for removal of ^{137}Cs from both alkaline and acidic waste solutions has been evaluated by workers at Sandia National Laboratories (C&EN 1992) (also see aa). This process could be competitive with commonly used organic ion exchangers such as Duolite CS-100 and inorganic exchangers such as zeolites for removing ^{137}Cs from alkaline wastes. Like hydrous titanates (see f), the crystalline titanates may also be modified to remove ^{90}Sr and TRU elements. Work to date has tested the crystalline titanates primarily using batch contacts. Calculations have shown that adding ^{137}Cs loaded crystalline titanates to glass feed would increase the number of canisters of HLW glass from 50 canisters (if a series of crystalline titanate columns were used) to 6,800 if a simple batch contact (in-tank) was used. The applicability of column contacts must be demonstrated. As noted in (aa), additional tests are needed to resolve this and other technical issues to determine if there are advantages to using crystalline titanates compared to using demonstrated cation exchange methods.

p. Use of Zeolites for Ion Exchange of ^{137}Cs in Alkaline Solutions

Use of zeolite ion exchange materials such as Linde IONSIV¹ IE-95, and IE-96 to remove ^{137}Cs from alkaline supernatant has been demonstrated (Bray et al. 1984). Zeolite materials have been chosen for ^{137}Cs removal from alkaline waste solutions stored at the former West Valley, New York, fuels reprocessing site. Zeolite materials typically exhibit large loading capacities and higher distribution factors for ^{137}Cs than do commonly used organic cation exchange resins such as Duolite CS-100. Zeolite resins cannot be eluted with HNO_3 because the ^{137}Cs loading capacity is destroyed by HNO_3 . The zeolite resins are thus typically considered for once-through use only, with the fully loaded resin column, considered direct feed to the HLW treatment (vitrification) process. Additionally, multiple uses of these

¹Linde IONSIV is a registered trademark of Union Carbide Corp., Danbury, Connecticut.

resins with alkaline solutions causes some degradation of the aluminosilicate structure with formation of gels and/or fines. Zeolite contains significant quantities of aluminum, silicon, and sodium, which are limiting components in the glass feed. Approximately 900 additional canisters of glass were estimated for vitrification of loaded zeolite resin from processing CC waste (Holten 1992). Up to 5,000 additional canisters would result from treating double-shell slurry and/or double-shell slurry feed. If batch contacts rather than column sorbtion methods were used, much higher glass volumes would result.

q. Use of Savannah River Site Resorcinol Resin for Removal of ^{137}Cs

Removal of ^{137}Cs from alkaline solutions has been studied at both the Hanford Site and SRS using organic cation exchangers. Most of the Hanford Site development has been centered on use of Duolite CS-100 using an elution (resin regeneration) method. Cesium removal from SRS waste will initially be performed using tetraphenyl boron precipitation; however, extensive studies have been performed at SRS using a resorcinol-formaldehyde resin for backup to the precipitation method. The resorcinol resin is also being considered for Hanford Site wastes as a possible replacement for Duolite CS-100. The manufacturing site for Duolite CS-100 has shifted to an alternate location with some loss of quality control. In particular, the 'new' Duolite CS-100 resin shows as much as 25 percent less capacity than the 'old' Duolite CS-100. Laboratory experiments show that the resorcinol resin has a higher ^{137}Cs capacity than Duolite CS-100. However, the resorcinol resin appears to exhibit poorer radiation stability than does Duolite CS-100. Because of the higher selectivity of resorcinol resin for ^{137}Cs , a once-through multiple column ion exchange scheme using columns of resorcinol resins has been considered with direct feed of the loaded resins to the glass melter, and minimal impact to glass volumes. The potential for replacing the reference Duolite CS-100 with the SRS resorcinol-formaldehyde resin should be studied further using both once-through and resin regeneration methods.

r. Removal of ^{137}Cs from Alkaline Solutions Using Solvent Extraction

Various solvent extraction processes for removal of ^{137}Cs from alkaline media have been demonstrated on a bench scale and in some cases, pilot-plant scale (Schulz and Bray 1987). Reagents tested for alkaline side solvent extraction of ^{137}Cs include the following:

- BAMBP¹
- Dipicrylamine - trinitrobenzene
- Tetraphenylboron - methylisobutylketone
- Polybromides - nitrobenzene
- Polyiodides - nitrobenzene
- 2-Thenoyltrifluoroacetone
- Crown ethers.

¹4-sec-butyl-2-(a-methylbenzyl)phenol

Alkaline side solvent extraction processes are often difficult to perform because of the tendency to form aqueous organic emulsions and resulting difficulties with phase separations, and extensive formation of third phase scums. For many processes, highly polar solvents are necessary to ensure adequate phase separations; many of these solvents (nitrobenzene, methylisobutylketone) are highly toxic.

s. Removal of ^{99}Tc from Alkaline Solutions Using Solvent Extraction.

Technetium, which exists as the pertechnetate (TcO_4^-) anion in both alkaline and acidic waste solutions, is extremely mobile in the environment. Thus, further evaluation and analysis of near-surface waste disposal systems may show that ^{99}Tc needs to be removed from some DST and SST wastes.

Removal of ^{99}Tc from alkaline solutions using strong base anion exchange resins was developed and demonstrated on a plant scale at the Hanford Site (Beard, Caudill 1964). Because the $^{99}\text{TcO}_4^-$ is held so tightly by the resin, strong HNO_3 solutions are required for elution. The need to recover and reuse HNO_3 is a disadvantage to anion exchange resin removal of ^{99}Tc from alkaline solutions.

Several organic compounds, including pyridine, tetrapropylammonium hydroxide in methylisobutylketone, and cyclohexanone are known, to extract TcO_4^- from highly alkaline waste solutions. Of these reagents, cyclohexanone is currently considered the most suitable reagent for removal of ^{99}Tc from Hanford Site solutions based on laboratory-scale tests by Schulz (1980). The Schulz (1980) work showed that distribution coefficients of TcO_4^- between aqueous NaNO_3 - NaOH solutions and cyclohexanone were sufficiently high to permit satisfactory countercurrent plant-scale extraction of $^{99}\text{TcO}_4^-$. Additionally, $^{99}\text{TcO}_4^-$ can be removed from cyclohexanone extracts by simple stripping with water, thereby eliminating the need to provide capital facilities for concentrating or destroying large amounts of HNO_3 .

Because a solvent extraction method from alkaline solutions has not been demonstrated on a large scale, anion exchange was chosen for evaluation in the technical options study. In addition, solvent extraction processes in alkaline systems are typically avoided because of the tendency to form emulsions, resulting in difficulties with phases separations and possible column flooding when using pulse columns. Methods that use organic solvents supported on a solid substrate may exhibit better separations characteristic for removal of ^{99}Tc from alkaline solutions (see Chapter 7.0).

t. Ozone

Ozone, O_3 , is a powerful oxidant in either acidic or alkaline media. Large amounts of ozone are used annually in water purification activities to destroy (oxidize) trace amounts of all kinds of organic compounds. Lutton and his colleagues (Lutton et al. 1979) demonstrated in the 1980's that ozone would oxidize complicated complexants such as HEDTA and

glycolic acid to similar molecules such as oxalate and acetate ions. Oxalate and acetate ions, so-called 'refractory' organic compounds, are typical end products in ozone oxidation systems.

Engineering considerations are highly important in realizing plant-scale ozonation operations. For example, detailed consideration must be given to such factors as systems and economics for generating and distributing ozone to process vessels containing wastes with soluble organic compounds; to overall process time cycles; to types, amounts, and properties of solids, if any, generated during waste ozonation, etc. The fact that ozonation does not oxidize complex molecules completely to CO_2 , H_2O , and gaseous nitrogen products but only to substances such as oxalate and acetate ions must be carefully weighed. Wastes containing oxalate or acetate ions may not be suitable for some disposal methods.

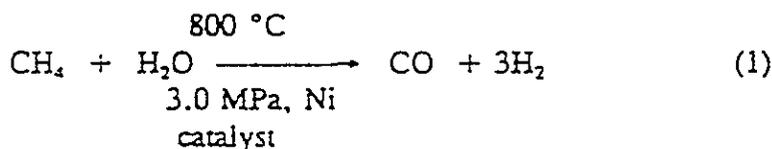
u. Wet Air Oxidation

Wet oxidation refers to a process in which aqueous Hanford Site tank wastes, containing soluble complex organic materials, are made 2-3M NaOH and then heated at a temperature below the boiling point of the aqueous waste. Under such conditions, the organic materials are oxidized to CO_2 , H_2O , and typically, low molecular weight compounds. Nitrate and nitrite ions in the waste serve as the source of oxygen for the oxidation process. For some wastes, it may be necessary to bubble air through the heated wastes to serve as an auxiliary oxidizer. Oxidation rates of organic molecules can often be increased by pressurizing the system.

The wet oxidation process represents a possible way of destroying organic complexants in Hanford Site wastes at temperatures considerably below those needed for an incineration process. High pressure reactors have been used industrially to oxidize organic molecules in various aqueous process wastes. A major technical concern about the application of wet oxidation technology to Hanford Site wastes centers on the corrosive and abrasive nature of such wastes. These aggressive conditions may seriously limit the useful life of small-diameter reactor equipment under high-pressure and high-velocity flow conditions.

v. Steam Reforming

That steam reacts at sufficiently high temperatures with volatile organic materials to produce CO , H_2 , and other gaseous products has long been known. So-called steam reforming of hydrocarbons (Equation 1) is one method of producing hydrogen:



Stream reforming has been suggested as a method for destroying organic materials dissolved in Hanford Site tank wastes. Conceptual fluidized bed schemes for performing such oxidation of complexants in alkaline tank wastes have been advanced. Potential serious drawbacks to technical feasibility of application of steam reforming oxidation of organic materials in Hanford Site wastes include the following: (a) the nonvolatility of EDTA and other complexants in the waste and (b) known poor flow characteristics of NaNO_3 -containing wastes in high-temperature fluidized bed calciners.

x. Crown Ether In Normal Paraffin Hydrocarbon

Several macrocyclic compounds, e.g., crown ethers, are known that extract ^{137}Cs to at least some degree from aqueous acidic as well as alkaline media. A major disadvantage of almost all these crown ethers is that they are essentially insoluble in normal paraffin hydrocarbons (NPH) or pure dodecane, preferred diluents for nuclear applications. Most bench-scale studies of such cesium extractants have employed aromatic or chlorinated aromatic compounds as diluents for the crown ether.

Dr. E. P. Horwitz at the Argonne National Laboratory has reputedly developed a cesium extraction system that employs a commercially-available crown ether soluble in NPH. Horwitz calls this extraction process the CSREX process; none of the details of the CSREX process have been published. It is believed that the CSREX process solvent includes three components. A crown ether, NPH, and a third component, possibly TBP, to promote solubility of the crown ether in NPH. It is also believed that the CSREX process will selectively and efficiently extract ^{137}Cs from strongly acidic nuclear waste solutions.

It should be noted that the CSREX process is just in its infancy. Much more bench-scale testing with both simulated and actual wastes is needed. If warranted, pilot plant-scale tests of the CSREX process with simulated and, perhaps, actual waste solutions also need to be performed. If all this testing is successful, then the CSREX process may be the preferred technology for removal of ^{137}Cs from acidified Hanford Site wastes.

y. EICrom - Actinides

EICrom Industries, Naperville, IL, manufactures TRU-spec resin, a macroporous polymeric resin impregnated with a mixture of CMPO and TBP. The composition of TRU spec resin is 13 wt% CMPO, 27 wt% TBP, and 60 wt% resin.

TRU spec resin is specifically designed for use in extraction chromatographic processes. Extraction chromatography is a separations process that combines the selectivity of solvent extraction with the simplicity and multistage attributes of traditional fixed-bed chromatographic systems. Advantages sometimes claimed for extraction chromatographic processes over liquid-liquid extraction systems include the use of simple process equipment and lower capital costs for process equipment. Despite these perceived advantages, to date, extraction chromatographic systems have not been selected to accomplish plant-scale nuclear separations processes.

Barney and Cowan (1992) recently conducted both batch and column experiments to study the extent and rate of uptake of Am(III) and Pu(IV) and other components, e.g., Fe(III), Bi(III), and lanthanides by TRU spec resin from simulated Hanford Site waste solutions. Results of these studies are exactly those expected from consideration of the known properties of CMPO liquid-liquid extraction systems. Thus, americium and plutonium decontamination factors are high enough to reduce the TRU element concentration of acidified SST wastes to or below 100 nCi/g of waste. But, the capacity of the TRU spec resin for sorbing americium and plutonium is severely decreased by the presence in the feed of certain metal ions, e.g., Fe(III), Bi(III), U(VI), and by high concentrations of HNO₃, all of which compete for CMPO molecules in the resin.

Experimental work has not yet been performed to determine the benefits, if any, of adding oxalic acid to feed solutions to suppress sorption of iron, bismuth, uranium, etc. If positive results are obtained when such experimental work is completed, the EICrom TRU spec resin may find useful plant-scale application in pretreatment of some Hanford Site wastes.

aa. Crystalline Titanates

Most of the ¹³⁷Cs in Hanford Site DST and SST wastes is in highly alkaline solutions. But, some ¹³⁷Cs may also be tightly incorporated in solid sludges in these tanks. Dissolution of washed, retrieved sludges in acid media thus may yield highly acidic, i.e., >1M, solutions containing ¹³⁷Cs. Two potential methods for direct removal of ¹³⁷Cs from acidic media are currently available: (1) liquid-liquid solvent extraction, e.g., CSREX process, and (2) sorption on crystalline sodium titanate. Alternatively, acidic wastes may be neutralized and ¹³⁷Cs removed by well-known inorganic or organic ion exchange technology from the alkaline supernatant liquid.

Crystalline titanates, also known as silico-titanates, are a relatively recent product developed by R. G. Dosch., Sandia National Laboratory, and R. C. Anthony, Texas A&M University. This product is a result of continuing studies, since the 1970's, on the properties and applications of titanates, both hydrous and crystalline.

Hydrous titanate ion exchanger is known from work at the Hanford Site and SRS to be highly effective in removing strontium and plutonium from highly alkaline wastes. Crystalline titanates are also reported (Chem. Eng. News 1992) to specifically and effectively sorb ¹³⁷Cs from alkaline media.

Sandia National Laboratory researchers also claim that crystalline titanate will specifically sorb ¹³⁷Cs from strongly acidic media. But, to date, there are no experimental data with actual Hanford Site acidified wastes to substantiate this claim. There are also some realistic and legitimate concerns about (1) capacity of the crystalline titanate for sorbing ¹³⁷Cs, (2) the specificity of the crystalline titanate for cesium, (3) the maximum and optimum HNO₃ concentrations in the feed solution, (4) the long-term stability and hydraulic

performance of crystalline titanate, and (5) commercial availability of the titanate at an affordable price.

The outstanding technical issues can only be properly resolved by extensive experimental work with simulated and actual Hanford Site wastes. Results of such research, when available, may offer convincing proof of the utility and superiority of crystalline titanates for removing ^{137}Cs , when and if required, from acidified Hanford Site wastes.

bb: Work in progress.

cc. Oxalates

The oxalate ion is well known for its ability to precipitate +3 and +4 actinides and +3 lanthanides from dilute HNO_3 solutions. For example, $\text{Pu}(\text{C}_2\text{O}_4)_2$ is often precipitated from purified $\text{Pu}(\text{NO}_3)_4$ solution as an intermediate in the preparation of purified plutonium dioxide.

Burney and Porter (1967) published results of experiments to determine the solubility of $\text{Pu}(\text{III})$ and $\text{Am}(\text{III})$ as a function of HNO_3 and oxalic acid concentrations. The solubility of both trivalent actinides increases with increasing HNO_3 concentration and decreasing total oxalic acid concentration. The solubility data of Burney and Porter indicate that, even under the most favorable conditions, the concentration of $\text{Am}(\text{III})$ in HNO_3 media cannot be reduced to or below 100 nCi/g by a single precipitation of $\text{Am}_2(\text{C}_2\text{O}_4)_3$. Of course, the solubility of americium and plutonium oxalates in acidified Hanford Site tank wastes is a complex function of several variables. These variables include waste HNO_3 concentration, ionic strength, concentration of anions (e.g., fluoride) that might complex $\text{Am}(\text{III})$ and $\text{Pu}(\text{IV})$, the concentration of metal ions, such as iron and zirconium, that complex the oxalate ion, and the concentration of fission product rare earths that will coprecipitate with the actinides. Thus, experimental work to determine the solubility of TRU element oxalate in actual waste solutions needs to be investigated.

Note should also be made of the Oxalate Precipitation Ion Exchange (OPIX) process developed by Forsberg (1980) and others at the Oak Ridge National Laboratory in the early 1980's for removal of actinides from PUREX process HLW. The OPIX process involves three major steps:

1. Operation of an improved PUREX process to recover as much as 99.99 percent of the uranium and plutonium and at least 95 percent of the neptunium in the irradiated fuel
2. Removal of the americium, curium, and rare earths in the PUREX process raffinate by precipitation of their oxalates
3. Cation exchange resin recovery of residual actinides and lanthanides in the mother liquor from the oxalate precipitation step.

Forsberg's tests with simulated PUREX process ($2M$ HNO_3) waste showed that >90 percent of the trivalent lanthanides and actinides were removed by precipitation of their oxalates in a continuous flow system.

Applicability of the OPIX process to remove TRU elements from acidified Hanford Site wastes has not yet been determined. Experimental work to determine such applicability appears worth doing.

dd. Lanthanum Fluoride Precipitation

A lanthanum fluoride precipitation procedure was first used historically to establish the existence of two oxidation states of neptunium and plutonium and also in the first isolation of plutonium. A lanthanum fluoride precipitation cycle was also an important tail end part of the $BiPO_4$ precipitation process.

All actinide +3 and +4 fluorides are insoluble in aqueous $1M$ H^+ solutions. Thus, in principle, addition of HF or other fluoride to acidified Hanford Site tank wastes will quantitatively precipitate TRU and lanthanide fluorides. High final concentrations, e.g., 1 to $3M$ of fluoride ion, may be necessary to achieve the necessary removal of TRU elements. After separation from the TRU element-free supernatant, the lanthanum-actinide fluoride precipitate can be solubilized by dissolution in a $1M$ HNO_3 - $Al(NO_3)_3$ (or H_3BO_3) solution or by metathesis to hydroxides (by treatment with KOH solution) that readily dissolve in HNO_3 . The final solution thus obtained will likely contain at least some calcium as well as ^{90}Sr .

Not only is the lanthanide-actinide fluoride precipitation process a cumbersome batch method, but it also suffers two major disadvantages compared to precipitation of lanthanide-actinide oxalates. Equipment selection is a problem because of the corrosive nature of HNO_3 - F^- solutions. Also, disposal of large volumes of solutions, free of TRU elements, but containing 1 to $3M$ fluoride ion, presents special difficulties.

ee. Antimonic Acid

One of the most challenging problems for nuclear separations chemists is to devise procedures for selective removal of ^{90}Sr directly from strong, i.e., $>1M$ HNO_3 , solutions. The current best available technology for accomplishing this task is the SREX liquid-liquid extraction process recently developed by Horwitz and associates at the Argonne National Laboratory.

Only crystalline antimonic acid, of all known inorganic ion exchange materials, selectively sorbs ^{90}Sr from highly-acidic nuclear waste solutions. The composition of crystalline antimonic acid approaches $Sb_2O_5 \cdot 4H_2O$ at room temperature, and the mole ratio of H_2O/Sb_2O_5 decreases with increasing drying temperature.

Several foreign investigators have conducted experimental work to study application of crystalline antimonic acid for selectively sorbing ^{90}Sr from a variety of acidic wastes. Results of these studies are referenced by Abe (1982). Partially as the result of these early studies, one or two small chemical companies in France produced and sold gram-to-kilogram amounts of crystalline antimonic acid.

Also, in the 1970's, Pacific Northwest Laboratory scientists studied potential application of crystalline antimonic acid for use in Hanford Site B Plant operations. Such use was rejected for the following reasons.

- No suitable reagent for eluting ^{90}Sr from loaded antimonic acid sorbent has ever been identified. Strontium is held so tightly that it cannot be eluted by either weak or strong acids or by weak or strong bases; even solutions containing complexing agents such as EDTA do not elute strontium.

Silver nitrate solutions can be used to elute strontium sorbed onto crystalline antimonic acid. But, primarily because of cost, silver nitrate eluents are not considered practical in plant-scale applications.

- Plant-scale quantities of crystalline antimonic acid may not be available.
- High cost of crystalline antimonic acid is a major deterrent to its use on a once-through basis.

ff. Phosphotungstic Acid Precipitation Process

Cesium phosphotungstate (PTA) is only slightly soluble in $1M$ HNO_3 solution. Two cesium salts can be isolated, namely, tricesium phosphotungstate ($\text{Cs}_3\text{PW}_{12}\text{O}_{40} \cdot 2\text{H}_2\text{O}$) that is preferentially precipitated at a PTA/cesium mole ratio < 0.33 , and the less soluble dicesium phosphotungstate ($\text{Cs}_2\text{HPW}_{12}\text{O}_{40} \cdot 2\text{H}_2\text{O}$) that is formed exclusively at a PTA/cesium mole ratio > 0.5 .

Plant-scale recovery of ^{137}Cs from PUREX Plant current acid waste (CAW) was routinely performed from April 1969 to September 1972. In plant-scale operation, a $0.1M$ PTA solution was added to the CAW to precipitate greater than 95 percent of the ^{137}Cs . ^{137}Cs was preferentially precipitated in a mixture of Rb^+ and K^+ ions. The soluble phosphotungstates of iron, zirconium, and aluminum did not interfere with precipitation of ^{137}Cs ; traces of these metals were removed by washing the cesium precipitate with dilute HNO_3 . The CsPTA precipitate was also washed three times with a $1.0M$ HNO_3 - $0.2M$ sodium gluconate solution to remove ^{90}Sr and other metal impurities. Finally, CsPTA solids were dissolved in $2.0M$ NaOH solution that was then centrifuged and stored for later treatment.

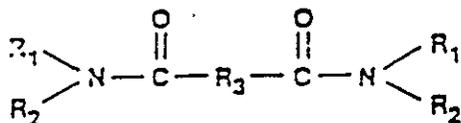
The CsPTA precipitation process, although operable on a plant-scale, has a number of disadvantages.

- It is a batch rather than a continuous process.
- It provides for recovery of only about 95 percent of the cesium in the feed.
- Phosphotungstate ion cannot be readily recovered from the dissolved CsPTA precipitate.
- Further chemical processing steps, e.g., ion exchange, are required to concentrate ^{137}Cs in the alkaline solution resulting from dissolution of the CsPTA precipitate.

Because of these disadvantages, well-known ion exchange technology is preferred for removal of ^{137}Cs from acidified Hanford Site wastes.

gg. Transuranic-Diamides

Bifunctional diamides are organic compounds of the general formula:



38210049.16

In formula 1, R_1 and R_2 are aliphatic hydrocarbons and R_3 is a bridging group between the two amide functionalities. Typically, R_1 and R_2 differ but they can be the same group; examples of R_1 and R_2 are CH_3 , C_3H_7 , and C_8H_{17} . Bridging groups can be very simple, e.g., CH_2 , or very complex, e.g., $\text{CH}-\text{C}_2\text{H}_4-\text{O}-\text{C}_{12}\text{H}_{25}$.

Because they contain two functional groups in the molecule, diamides extract +3 actinides as well as +4 and +6 actinides from strong HNO_3 solutions. Thus far, the properties of diamides for extracting actinides from acidic nuclear waste solutions have only been studied by C. Musikas and his colleagues at the French Fontenay-aux-Roses research laboratories outside Paris, France. For use in partitioning TRU elements from HLW and other wastes, French scientists and engineers prefer diamides over organophosphorus extractants because they think the following.

- Degraded diamides are completely incinerable.
- Generation of secondary aqueous solvent cleanup wastes can be eliminated because hydrolytic and radiolytic degradation products of diamide compounds are not inimical to process performance.

Experimental evidence to substantiate these claims has not yet been established.

A recent evaluation (WHC-EP-0577 [WHC 1993]) found that for removal of TRU elements from acidified Hanford Site wastes CMPO-based extractants currently have several major advantages over diamide-based extractants. These advantages are as follows.

- CMPO is commercially available in process-scale quantities; diamide TRU extractants are not.
- CMPO is a stronger actinide extractant; thus, smaller quantities of expensive reagent are required for the same degree of actinide extraction.
- CMPO efficiently extracts Am(III) and other actinides from 0.5 to 1M HNO₃ solutions as well as at higher aqueous phase acidities; diamides only extract Am(III) efficiently at aqueous phase HNO₃ concentration above about 3 to 4M.
- CMPO provides superior decontamination of TRU elements from Fe(III).
- CMPO resists deleterious acid hydrolysis degradation much more strongly than do diamides.

hh. Transuranic-Dihexyl-N,N-Diethylcarbamoylmethyl Phosphonate (CMP)

CMP, a commercially available reagent, has many of the same properties as CMPO. Thus, like CMPO, CMP solutions efficiently extract +3, +4, and +6 actinides from 0.5 to 5.0M HNO₃ solutions. But because it is a phosphonate compound, CMP is a less powerful actinide element extractant than is CMPO. Because of this property, both process advantages and disadvantages accrue when CMP is used in TRU element extraction processes. Thus, at equal organic phase concentrations, CMP solutions extract less Fe(III) and Bi(III) from HNO₃ feeds than do CMPO solutions. Additional properties of CMP-diluent solutions are presented in WHC (1993).

CMPO is currently preferred over CMP for use in extracting actinides from acidified Hanford Site wastes for three reasons.

- CMPO is a stronger actinide extractant; thus, smaller quantities of expensive reagent are required for the same degree of actinide extraction.
- There is much more successful bench-scale experience with CMPO extraction systems in extraction of actinides from actual waste solutions.
- The fundamental properties of CMPO as an actinide extractant are more well known and understood.

But, should future circumstances warrant, CMP could be substituted for CMPO in a waste pretreatment plant without necessitating expensive changes in either equipment or process operation.

jj. Dibutylbutylphosphonate

Dibutylbutylphosphonate (DBBP) is a neutral, monofunctional organophosphorus compound. Like other monofunctional reagents, DBBP is a powerful extractant for Am(III) but only from low acid (pH > 2) highly salted nitrate solutions. Advantage of this chemistry was taken at the Hanford Site to develop and operate a 30 vol% DBBP-CCl₄ solvent extraction process for recovery of ²⁴¹Am and plutonium from PFP waste. Throughout the entire time it was operated, the DBBP process was plagued by great difficulties with control of feed pH by on-line addition of 50 wt% NaOH to an unbuffered waste.

Experience at the Hanford Site with the DBBP extraction process emphasizes that TRU element separation processes that accommodate 1 to 4M HNO₃ feed solutions generated from dissolution of tank sludges are preferable to those that require adjustment of feed acidity to < 0.5M HNO₃. Adjustment of dissolved sludge solutions to < 0.5M HNO₃ is objectionable for two reasons. Lack of buffering capacity in such solutions makes it very difficult to control the TRU element separation process feed pH in the necessary range. Secondly, neutralization of excess HNO₃ in dissolved sludge solutions may result in precipitation of actinide-bearing solids, e.g., Fe₂O₃•xH₂O, that must be removed and treated separately.

kk. Cobalt Dicarbolide: Cesium and Strontium

For over 15 years, Kyrs, Rais, Selucky, and their associates at the Nuclear Research Institute in (then) Czechoslovakia have pioneered use of the compound 'Cobalt Dicarbolide,' H⁺{[PI-(e)-1,2-B₉C₂H₁₁Cl₂]₂Co}⁻, in solvent extraction of ¹³⁷Cs from strong HNO₃ solutions (Schulz and Bray 1987). Small concentrations of dicarbolide dissolved in a polar solvent such as nitrobenzene effectively and preferentially extract cesium from aqueous 0.5 to 1.0M HNO₃ solutions. Under these conditions, ion pairs, e.g., Cs B (B = {[PI-(e)-1,2-B₉C₂H₁₁Cl₂]₂Co}⁻), exist in the organic phase. Kyrs et al. have established that Cs⁺ can be readily stripped from the dicarbolide-nitrobenzene phase by strong, i.e., > 3M HNO₃, acid solutions.

Results obtained by Kyrs et al. indicate dicarbolide-nitrobenzene solutions will also extract ⁹⁰Sr very efficiently from aqueous 0.5 to 3.0M HNO₃ solutions provided a suitable complexing agent, e.g., a polyethylene glycol (PEG) compound containing the chemical moiety, -P(O)-CH₂-P(O)-, is added to the aqueous phase. The Czech workers preferred an inexpensive and commercially-available PEG sold (in the 1980's) in Czechoslovakia under the trade name Slovafo 909. Strong (i.e., > 3M HNO₃) solutions strip divalent strontium from the dicarbolide-nitrobenzene phase. Use of the affinity of H⁺CoB₂-nitrobenzene solutions for Sr²⁺ has been made in devising analytical procedures for ⁹⁰Sr in biological media.

Other items of interest in consideration of the use of dicarbolidides for extraction of ^{137}Cs and/or ^{90}Sr include the following:

- Hundreds of kilograms of cobalt dicarbolidide have been synthesized in Czechoslovakia.
- Cobalt dicarbolidide is only slightly soluble in aqueous solutions.
- Cobalt dicarbolidide appears to be quite resistant to either chemical or radiolytic degradation.
- Russian investigators are reported to have successfully tested dicarbolidide extraction of ^{137}Cs and ^{90}Sr from full-level PUREX process HLW on a plant-scale.
- Essentially no experimental work with dicarbolidide extractants has been performed in the U.S. This situation may change shortly as the result of ongoing discussions between the DOE and Russian officials on ways to enhance U.S.-Russian joint technical efforts.

The current overriding technical disadvantage of the cobalt dicarbolidide extraction process is the need to use toxic nitrobenzene or similar compound, e.g., dichloroethane, as a diluent. There is also concern on the part of some U.S. technical experts that radiolytic degradation of the cobalt dicarbolidide extractant will produce chloride ion that, in the presence of 1-3M HNO_3 , will act to corrode stainless steel equipment. Until these technical issues have been resolved, other cesium-strontium removal technologies are likely to be preferred.

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APPENDIX D

EXCERPTS FROM TANK WASTE TECHNICAL OPTIONS REPORT,
WHC-EP-0616, REV. 0, 1993
(WASTE TREATMENT FOR ONSITE DISPOSAL LOW-LEVEL WASTE)

8.2 TECHNICAL OPTION SELECTION
G1.1 TECHNICAL OPTION SELECTION
G17.0 REFERENCES

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8.2 TECHNICAL OPTION SELECTION

The near-surface disposal alternatives discussed in this section were initially identified by a literature review of practices and technology for the disposal of high-level radioactive waste (HLW), low-level radioactive waste (LLW), and hazardous waste. The literature review was supplemented with the waste management expertise of the staff and formal technology workshops. The literature included a number of previous and current waste form surveys (Arniella and Blythe 1990, Crisler 1980, DOE 1981a, DOE 1981b, DOE 1982, IAEA 1988, Kalb and Columbo 1983, Kibbey and Godbee 1980, Lutze and Ewing 1988, Schulz et al. 1980, Treat et al. 1980, Tucker et al. 1983, and Wiemers et al. 1992).

Figure 8-1 shows the waste treatment technical options and highlights those that are evaluated in this chapter. Appendix H provides a more detailed discussion of the process by which options were selected for evaluation.

The intent was to first identify the waste form and then to specify a process. These treatment processes were organized, based on their material properties and unit processes, into groups. Group characteristics were then used to organize the treatments into a framework for the overall diagram (Figure 8-1). The first obvious division was to separate low-temperature processes from high-temperature processes. In general, low-temperature processes do not chemically change the waste components, whereas the high-temperature processes, i.e. the glass and ceramic processes, do change the waste components. The division between high and low-temperature processes was set at 500 °C (932 °F), the point at which the use of exotic metals and ceramics in process equipment becomes a consideration. The low-temperature processes identified in the literature consisted of cement and silicate grouts, and organic polymers such as bitumen and polyethylene. The high-temperature processes consisted of glass and ceramic processes.

The overall diagram was examined for logic pathways (i.e. treatments) that were not identified by the initial literature review. For example, denitration of the waste in conjunction with a grouting process is not readily identified by a literature survey of waste disposal and treatment processes. Using this logic, a parallel path for low-temperature processes that linked denitration with grouts and organic polymers was generated. A logical alternative to organic polymer forms are inorganic binders. However, no suitable inorganic binders were identified from the literature. These logic pathways implied new treatments to be considered. These pathways, although logical, will in many cases propose treatment processes that are inferior or that offer no advantage. Examples of logical, but inferior, processes would be, to put sodium nitrate salts directly into sulfur, or to put ceramic pellets into bitumen. A sodium nitrate/sulfur waste form would be unsuitable due to flammability concerns, and use of a bitumen binder on ceramic pellets would offer no processing or waste property advantage to a ceramic form.

The basic high-temperature processes of glass and ceramic, when examined in detail included subsets such as monoliths, sintered powders, calcine, and marbles or pellets. The coating and embedding of glass marbles in metal is also discussed in the literature. The

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logical extension of metal matrix process is to consider organic, grout, and inorganic matrixes. Modified sulfur, an inorganic material was identified as being compatible with glass or ceramic and was included as a matrix material.

Once the logic diagram was assembled, representative treatments were identified for evaluation. Treatments were passed over for evaluation only when it could be shown using the available information that the selected processes of the same general type were superior or not sufficiently different such that the technology group is not fairly evaluated. Evaluation of a treatment process by the systems engineering approach requires a minimum level of development to define the process and waste form. Thus treatments were also passed over if properties of the waste form were not published or equipment to achieve necessary process operations could not be identified.

Starting from the top of the diagram, the four basic waste forms were grouts, organic polymers, inorganic binder, and mineral precipitation. Sulfur, the only inorganic binder identified, is considered incompatible with nitrate salts. Mineral precipitation is not an effective treatment for the waste components generally found in solution. Two organic polymers were identified, bitumen and polyethylene. Both are thermoplastic materials. No applications of thermoset materials for waste treatment were found in the literature. Thermoset materials do not appear to offer any advantage over bitumen or polyethylene. The Hanford cement grout process was selected as the base grouting technology. Based on a cursory review, silicate grouts did not offer any significant advantage over cement based grouts. Organic polymer waste forms were identified as being unique from grouts and having superior leach rates. The polyethylene waste forms exhibit properties that are superior to bitumen.

Of the denitration processes identified, calcination was identified as being the most effective at nitrate destruction. A mineral precipitation/grout process was considered to be unique from the other processes selected for evaluation. Direct grouting of calcined material was considered to be technically difficult due to the chemical incompatibility concerns. Use of organic polymers with calcine is not considered unique from a salt/polyethylene waste form and would result in a similar evaluation.

The high-temperature forms include glass, ceramic and calcine. Calcine was excluded from consideration because its leach rate is greater than grout. A glass casting process was selected to represent this technology. Ceramic processes are expected to have similar performance and costs but the technology is less developed. Application of the soil melt slurry injection technology to treatment of retrieved waste is considered to be unique from the traditional vitrification processes.

Glass in a lead matrix was developed for vitrification of commercial HLW. The lead improved thermal conductivity and provided an additional barrier. For the subject LLW application, sulfur and grout were identified as candidate materials. Since glasses are not always compatible with grouts, the grout was evaluated in conjunction with a ceramic waste form.

The selection of representative treatments from the logic diagram is not intended to absolutely foreclose consideration of passed over treatments. If, for example, it is concluded that monolithic glass forms are the preferred treatment, then the characteristics that make this a desirable treatment are to be reviewed and other waste forms such as monolithic ceramic forms need to be reconsidered. However, if the salt/polyethylene waste form or process, for example, is found to be generally unsatisfactory, then further consideration of alternate organic polymers to encapsulate dried salts should not be necessary.

The logic diagram is not expected to show every single manufacturing material or even to include every single material that has been proposed or tested for waste disposal. The logic diagram, however, is expected to include those waste forms that are viable processes for sodium nitrate wastes.

The logic diagram serves as the initial screening of treatment processes for evaluation. As new data become available and as new treatment concepts are proposed and developed it will be necessary to update the logic diagram. If a new concept is found to be sufficiently unique, it will be necessary to evaluate it against the performance, cost, complexity, and development status of whatever technology is the current baseline.

H1.0 TECHNICAL OPTION SELECTION

The near-surface disposal alternatives discussed in this section were initially identified by a literature review of practices and technology for the disposal for high-level radioactive waste (HLW), low-level radioactive waste (LLW), and hazardous waste. The literature review was supplemented with the waste management expertise of the staff and formal technology workshops. The literature included a number of previous and current waste form surveys (Arniella and Blythe 1990; Crisler 1980; DOE 1981a, 1981b, 1982; IAEA 1988; Kalb and Columbo 1983; Kibbey and Godbee 1980; Lutze and Ewing 1988; Schulz et al. 1980; Treat et al. 1980; Tucker et al. 1983; Wiemers et al. 1992). The more comprehensive surveys are listed at the end of this section. Figure H1-1, Onsite Disposal Technical Option Selection, shows the waste treatment technical options and highlights those that are evaluated in this appendix.

The logic used to create Figure H1-1 was to first identify the waste form and then to specify a process. These treatment processes were organized, based on their material properties and unit processes, into groups. Group characteristics were then used to organize the treatments into a framework for the overall diagram (Figure H1-1). The first division was to separate low-temperature processes from high-temperature processes. In general, low-temperature processes do not chemically change the waste components; whereas, the high-temperature processes (i.e., the glass and ceramic processes) do. The division between high- and low-temperature processes was set at 500 °C (932 °F), the point at which the use of exotic metals and ceramics in process equipment becomes a consideration. The low-temperature processes identified in the literature consisted of cement and silicate grouts, as

well as organic polymers (such as bitumen and polyethylene). The high-temperature processes consisted of glass and ceramic processes.

The overall diagram was examined for logic pathways (i.e., treatments) that were not identified by the initial literature review. For example, denitration of the waste in conjunction with a grouting process is not readily identified by a literature survey of waste disposal and treatment processes. Using this logic, a parallel path for low-temperature processes that linked denitration with grouts and organic polymers was generated. A logical alternative to organic polymer forms is inorganic binders. However, no suitable inorganic binders were identified from the literature. These logic pathways implied new treatments to be considered. These pathways, although logical, will propose in many cases treatment processes that are inferior or that offer no advantage. Examples of logical, but inferior, processes would be to put sodium nitrate salts directly into sulfur or to put ceramic pellets into bitumen. A sodium nitrate/sulfur waste form would be unsuitable because of flammability concerns, and use of a bitumen binder on ceramic pellets would offer no processing or waste property advantage over a ceramic form.

The basic high-temperature processes of glass and ceramic, when examined in detail, include subsets such as monoliths, sintered powders, calcine, and marbles or pellets. The coating and embedding of glass marbles in metal is also discussed in the literature. The logical extension of the metal matrix process is to consider organic, grout, and inorganic matrixes. Modified sulfur, an inorganic material, was identified as being compatible with glass or ceramic and was included as a matrix material.

Once the logic diagram was assembled, representative treatments were identified for evaluation.

The logic diagram does not show every manufacturing material or even include every material that has been proposed or tested for waste disposal. The logic diagram does include the waste forms that are viable processes for sodium nitrate wastes.

The logic diagram serves as the initial screening of treatment processes for evaluation. As new data become available and as new treatment concepts are proposed and developed, it will be necessary to update the logic diagram. If a new concept is found to be sufficiently unique, it will be evaluated against the performance, cost, complexity and development status of the current baseline technology.

Resource limitations required that the number of technologies evaluated in detail be kept to a small number. To meet with this limitation, only processes that are unique are evaluated. Treatments were not evaluated when it could be shown using the available information that the selected, similar processes of the same general type were superior or not sufficiently different, such that the technology group is not fairly evaluated. Evaluation of a treatment process by the systems engineering approach requires a minimum level of

development to define the process and waste form. Thus, treatments were also passed over if properties of the waste form were not published or equipment to achieve necessary process operations could not be identified.

As new data become available and new treatment concepts are proposed and developed, it will be necessary to update the logic diagram. If a new concept is sufficiently unique, it will be evaluated against the performance, cost, complexity, and development status of the current baseline technology.

- a. A number of methods are available to denitrate the waste. Use of chemical additives to denitrate the waste was not evaluated because chemical denitration is generally inefficient (on average, less than 90 percent nitrate is destroyed).
- b. Electrolytic denitration of alkaline nitrate solutions was tested by Hobbs et al. (1986). The presence of chromate ion inhibited the denitration process. Adding bismuth salts blocked the effect of chromate. Up to 95 percent of the nitrate could be destroyed with good electrical efficiency. Greater than 99 percent could be destroyed with significantly greater power consumption. The amount of bismuth added was not explained. Because of uncertainty with the impact on waste volume and toxicity, this option was not evaluated further.
- c. Calcine waste forms were not considered because of the high solubility of sodium oxide. Even if only sludges were calcined, the leach rate of the calcine would be higher than all other waste forms considered (Schulz et al. 1980).
- d. The only inorganic binders identified by the literature search were lead and sulfur cement. Sulfur cement is a U.S. Bureau of Mines developed construction material that has advantageous properties for waste treatment (Van Dalen and Rijplema 1989). Sulfur is not compatible with oxidizers such as sodium nitrate. A single citation was found on using sulfur in a one-step waste calcining to make a calcine/sulfur waste form. Acidic waste was calcined with the generation of large quantities of SO_2 and SO_3 in the offgas. The product was considered to be very leach resistant (Davis et al. 1962). This investigation used unmodified sulfur and was completed before the development of effective sulfur cement formulations. Calcined sodium nitrate (sodium oxide) is not expected to be compatible with sulfur cement as sodium oxide is extremely hygroscopic. It is probable that leach test results would be poor.

No citations could be found on the use of lead (or other metals) to immobilize waste salts, calcine, or mineral precipitates. The high density of metals relative to that of salts, oxides, and minerals would appear to make this impractical.

No high temperature in situ processes were identified other than in situ vitrification (ISV) that could be applied to this waste stream.

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- e. The waste loading, cost, and leach resistance of a salt/bitumen process are similar to those of a salt/polyethylene process. Polyethylene is superior to bitumen with respect to radiation resistance, softening temperature, and flammability (Kalb et al. 1991).

Use of organic polymers in conjunction with mineral precipitates would be similar to the salt/polyethylene process. Higher costs are expected because of the waste mass increase from mineralization.

No citations were found on the use of alternatives to thermoplastic organic materials (such as thermoset resins).

No citations were found on the use of organic polymers with a glass or ceramic waste form. No advantages to this process were identified.

- f. Denitration and grouting of sodium nitrate wastes will generate a grout made from a strong caustic solution (sodium hydroxide). Sodium hydroxide being composed of monovalent ions will not incorporate into the cement hydration structure and will readily leach from the product. The leachate and product are likely to fail the State corrosive material test.
- g. A number of processes have been proposed or studied for preparing multiphase crystalline ceramic waste forms. These include uniaxial hot pressing, hot isostatic pressing, cold pressing and sintering, and disc pelletization and sintering. While all of these processes are in use in commercial applications, only uniaxial hot pressing and hot isostatic pressing have been tested on a larger than laboratory scale for radioactive waste. Uniaxial hot pressing in bellow containers has been chosen for nonradioactive demonstration by the Australian nuclear program. Vitrification processes have been demonstrated and with radioactive waste and are in full-scale operation.
- h. Production of crystalline ceramic in a sintered powder, pellet, or clinker form has been suggested as a means to minimize the ceramic-forming development requirements for the ceramic-forming processes described previously in g. However, the high surface area exposed to leaching increases the release rate from the waste and, thus, is undesirable.
- i. Conversion of the sodium nitrate wastes to cancrinite wastes was studied (Barney 1975). Given the high surface area of this waste form and the resulting leach rate of nitrate, this form offers little improvement relative to the grout process.
- j. The leachate from hydraulic cements are alkaline. Glasses are subject to accelerated corrosion in the presence of alkaline solution. For this study, it has been hypothesized that it may be possible to formulate a ceramic that is more resistant to alkaline attack than typical radioactive waste glasses. (Tailored

ceramic phases are in general thermodynamically more stable than vitreous phases.) Thus, a sintered ceramic in grout technical option is included for evaluation as opposed to a glass in grout option.

- k. Grouting processes based on sodium silicate as the reactive agent are available from waste treatment service vendors. A silicate formulation is presumed to have performance properties comparable to those of Hanford Site grout formulations. A sodium silicate formulation is evaluated in conjunction with the mineral grout technology option.

A Hanford Site grout formulation tailored for the denitrated waste technical option is presumed to be similar to the Hanford Site grout technical option. Silicate and Hanford Site grout formulations are presumed to have similar performance properties.

- l. Two options for transport of the waste to the ISV site are transfer as a powder or transfer as a slurry. Transfer as a slurry is consistent with the present Hanford Site practice. No significant advantage for powder transport was identified. Because transfer as a powder departs from current Site practice, this option is not evaluated.
- m. Two inorganic matrix materials were identified in this study, lead and sulfur cement. Sulfur cement is a U.S. Bureau of Mines developed construction material that has advantageous properties for waste treatment. Lead has been proposed as a matrix to encapsulate container packaged glass marbles. Sulfur cement was selected over lead for evaluation because lead is a toxic material and sulfur cement is not. In addition, the relative specific gravity of the materials (lead > glass > sulfur cement) complicates use of lead. The high specific gravity of the lead will cause the glass to float on the lead.
- n. All processes under consideration manufacture several hundred cubic meters of waste form each day. Given the shielding requirements and logistics of packaging and transporting this volume of waste form, use of containers is generally considered to be impractical. Two technical options, salt/polyethylene and containerized glass are included to verify this assumption.
- o. The latent heat and low thermal conductivity of these waste forms result in extended solidification times for large masses such as would be formed by bulk disposal. It is possible that these waste forms would segregate by sedimentation during this time and thus form a less desirable product (low polymer to salt ratio.)
- p. Bulk handling of glass is only practical when in the form of cullet, marbles, etc. The glass in sulfur process incorporates a bulk glass cullet process.

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- q. Two inorganic matrix material were identified in this study, lead and sulfur cement (described previously in m). Application of the sulfur cement matrix to a ceramic form would generate a waste form analogous to the glass in sulfur waste form. Because radioactive waste vitrification technology is more developed than ceramic technology, the glass in sulfur option was selected.
- r. Sodium silicate- and cement-based grouts (described previously in j and k) are presumed to similar performance properties. The cement-based grout option was selected relative to a sodium silicate-based option because there is more data on cement-based formulations.

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APPENDIX E

EXCERPTS FROM TANK WASTE TECHNICAL OPTIONS REPORT,
WHC-EP-0616, REV. 0, 1993
(WASTE TREATMENT FOR OFFSITE DISPOSAL - HIGH-LEVEL WASTE)

9.2 TECHNICAL OPTION SELECTION
11.0 WASTE FORM
112.0 REFERENCES

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9.2 TECHNICAL OPTION SELECTION

The offsite disposal alternatives discussed in this section were initially identified by a literature review of practices and technology developed for the disposal of HLW. Technologies for LLW disposal were also reviewed for waste forms and processes potentially extendable to HLW use. The literature review was supplemented with the waste management expertise of WHC staff and formal technology workshops. The literature included a number of previous and current waste form surveys (DOE 1981a, 1981b, 1982; Kalb and Columbo 1988; Lutze and Ewing 1988; Schulz et al. 1980; Treat et al. 1980; Wiemers et al. 1992). The intent was to first identify the waste form and then to specify a process to generate that form. Figure 9-1 shows the waste treatment technology options and highlights those that are evaluated in this chapter. A more complete discussion on selection of the waste treatment options is provided in Appendix I.

The treatment processes were organized into groups, based on their material properties and unit processes. Group characteristics were then used to organize the treatments into a framework for the overall diagram (Figure 9-1). The first division separates low-temperature processes from high-temperature processes. In general, low-temperature processes do not chemically change the waste components, but merely immobilize them in solid form. By contrast the high-temperature processes generate new, usually more stable, products. The division between high- and low-temperature processes was set at 500 °C (932 °F), a temperature below which major chemical reactions do not occur with the waste and above which the use of exotic metals and ceramics equipment becomes a factor in the design and manufacture of process equipment. The low-temperature processes identified in the literature immobilize the waste in concrete or materials such as bitumen or aqueous silicate. The high-temperature processes incorporate the waste into oxide, glass, or ceramic products.

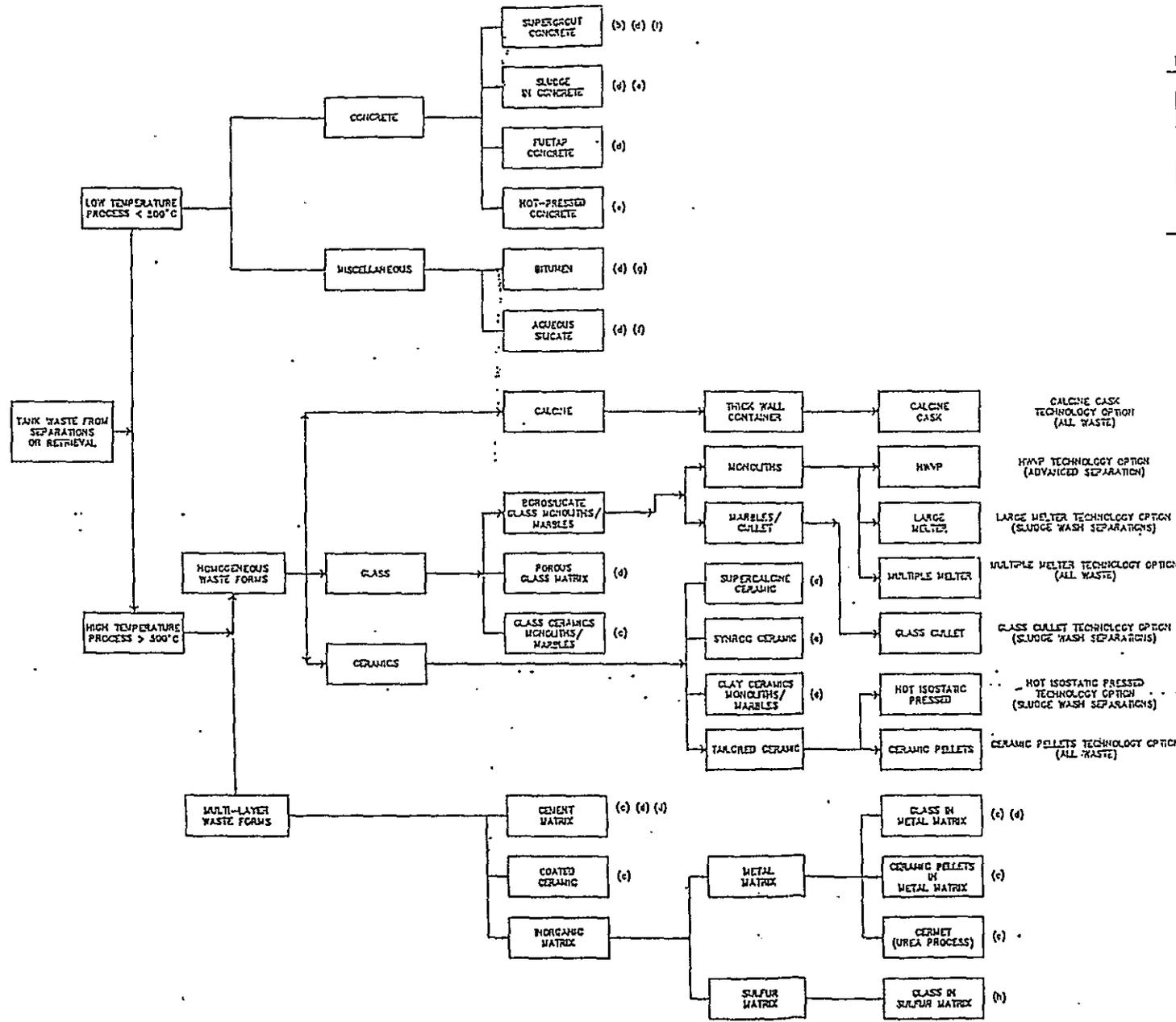
The overall diagram was examined for additional logic pathways (i.e., treatments) that were not identified by the initial literature review. Most of those identified were not incorporated in the diagram because they were inferior to processes already shown. For example putting sodium nitrate into sulfur is unsuitable since it creates a potential fire and explosion hazard, while the use of bitumen as a matrix for ceramic pellets offers no processing or waste property advantages compared with the ceramic form itself.

When examined in detail the basic high-temperature processes of glass and ceramic included subsets such as monoliths, sintered powders and marbles or pellets, which are included in the diagram.

The coating and embedding of glass marbles in metal matrices is discussed in the literature. A logical extension of the metal matrix process was to consider organic and inorganic (e.g., grout) matrixes. Modified sulfur was identified as being compatible with glass or ceramic and was included as a matrix material.

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Figure 9-1. Offsite Disposal Alternative Selection.



LEGEND

PROCESSES NOT EVALUATED

EVALUATED PROCESSES

- NOTES**
- (a). PROCESS AND WASTE FORM SIMILAR TO TAILORED CERAMIC.
 - (b). BULK PROCESS NOT APPLICABLE TO CONTAINERIZED FORMS.
 - (c). PROCESS COMPLEXITY HIGH.
 - (d). WASTE FORM VOLUME MORE THAN TWICE THAT OF GLASS MONOLITHS.
 - (e). PROCESS LIMITED TO LOW SOURCES WASTE. PROCESS IS LOW PRIORITY ALTERNATIVE TO VITRIFICATION AT HMWP.
 - (f). LEACHABILITY EXCEEDS BORO-SILICATE GLASS 100X.
 - (g). SUSCEPTIBLE TO DEGRADATION AT REPOSITORY TEMPERATURE.
 - (h). REPOSITORY ACCEPTANCE UNCERTAIN.
 - (i). GLASS SUSCEPTIBLE TO CORROSION AT HIGH pH OF CONDIT.

OFFSITE DISPOSAL TECHNOLOGY OPTION SELECTION

Once the logic diagram was assembled, representative treatments were identified for evaluation. Treatments were not evaluated when it could be shown that the chosen processes of the same general type were superior, or that the chosen waste form possessed equal or superior properties. Evaluation of a treatment process by the systems engineering approach requires a minimum level of development to define the process and waste form. Treatments were therefore passed over if properties of the waste form were not published or equipment to achieve necessary process operations could not be identified.

The four basic waste forms identified in Figure 9-1 are concretes, miscellaneous waste forms, homogeneous waste forms and multilayer waste forms.

The literature contained little information on concretes which was relevant to the particular waste forms which exist at the Hanford Site. Further, predicted waste form loadings were low and leach rates were high compared to other waste forms.

Two miscellaneous technologies were identified, bitumen and aqueous silicate. Bitumen presents a combustion hazard with high nitrate wastes (which are very common at the Hanford Site), while waste loadings for the aqueous silicate process were found to be low compared with other waste forms.

The homogeneous waste processes were divided into three different groups: glass, calcination, and ceramic products. The HWVP glass process was selected as the base glass technology, since it possesses the best developed, approved technology. The calcination process was selected on the basis of simplicity. A tailored ceramic was selected since it yields final waste forms at least as inert and durable as glass. For this application the mineral assemblage formed in the ceramic would contain nepheline, monazite, and corundum as major phases.

Multilayer waste forms were identified as being unnecessarily complex. The first processing stage typically produces a glass or ceramic product, while a second stage incorporates this waste form into a metal, cement, or inorganic matrix without any significant gain in performance.

The selection of representative treatments from the logic diagram is not intended to eliminate other treatment processes. For example, if monolithic glass forms are the preferred treatment, the characteristics that make this a desirable treatment must be reviewed and other waste forms, such as monolithic ceramic forms, should be reconsidered. If, however, the tailored ceramic waste form or process, for example, is found to be generally unsatisfactory, further consideration of alternate ceramic waste forms should not be necessary.

The logic diagram provides the initial screening tool for the evaluation of treatment processes. As new data become available and as new treatment concepts are proposed and developed, it will be necessary to update the logic diagram. If a new concept is found to

have sufficient merit, it will be necessary to evaluate it against the performance, cost, complexity, and development status of the technology which represents the current baseline.

The logic diagram is not intended to show every single manufacturing process, or even to include every single material, that has been proposed or tested for waste disposal. It is, however, developed to include those processes and waste forms that may be viable for disposal of HLW at Hanford.

II.0 WASTE FORM

The scope of this study examines glass and ceramic waste forms for encapsulation of high-level radioactive waste (HLW). The results determined from previous studies indicate that the Hanford Site HLW should be limited to glass, cements, and ceramics (Schulz et al. 1980). For this study, cements have been excluded based on repository cost and public acceptance. Figure II-1 identifies different waste forms for offsite disposal.

Evaluation of a thick-walled container or cask is being examined in connection with a calcined waste form. This calcine-cask system, which is not addressed by Schulz et al. (1980), is based on the integrity of the storage container. This logic is consistent with that of spent fuel storage.

The options identified within the study have concurrence from the National Academy of Sciences (NAS).

II.1 BOROSILICATE GLASS

Borosilicate glass is a waste form in four treatment options: Hanford Waste Vitrification Plant (HWVP), large melter, multiple melter, and glass cullet.

II.1.1 Formulation

The formulation of the waste form depends on the feed stream oxides. A 25 wt% oxide loading is assumed for HWVP, large melter, and glass cullet. These processes match wastes that have been processed to minimize HLW volume as well as reduce sodium and metal oxide content. The multiple melter is not linked to separations technology. Thus, the feed to the multiple melter is high in sodium, which becomes the controlling parameter, because processing requirements limit the glass to 15 wt% sodium oxide. For some feed streams, the oxide loading could be slightly higher (Watrous et al. 1991). Ten components within the feed stream will be analyzed to determine the composition of the frit. The 10

components are SiO_2 , B_2O_3 , Na_2O , Li_2O , CaO , MgO , Fe_2O_3 , Al_2O_3 , ZrO_2 , and other oxides with a weight fraction greater than 0.001.

The variation of the frit composition will be modeled based on feed stream oxide compositions and control of physical properties of the final glass waste form. Based on this assumption the frit composition was limited to four components: SiO_2 , B_2O_3 , Na_2O , and Li_2O . Silicon dioxide is to provide glass durability. The other glass formers selected aid in lowering the melting temperature of silica. A small quantity of sodium oxide is added to allow for introduction of additional alkali into the glass and to provide flexibility for a high sodium waste feed. Lithium oxide and boron trioxide are provided to adjust for viscosity and electrical conductivity. Boron also provides chemical durability that is thought to help stabilize certain elements in the glass phase (Lutze and Ewing 1988).

II.1.2 Quantities Made

The amount of glass made and placed into canisters will be determined by the separations technology combined with the glass process.

Table II-1 identifies the number of canisters that would be produced using different separations treatments combined with a glass treatment option. A larger canister where indicated is the basis for the option to produce less canisters as shown by Table II-1.

Table II-1. Glass Process Canister Production Estimates.

Process	Separations technology used	HWVP canister (0.6 m dia. x 3.17 m h) (number)	Large canister (0.68 m dia. x 4.76 m h) (number)	Shielded cask (2.13 m dia. x 5.79 m) (number)
HWVP	Solvent extraction	11,300*		
Large melter	Sludge wash	37,700	16,800*	
Multiple melter	None	364,000	160,000*	
Glass cullet	None	50,000		3,100*

* Container size assumed in process evaluation.
HWVP = Hanford Waste Vitrification Plant

II.1.3 Physical Properties

Borosilicate glass is a very durable waste form. Waste oxides are in a homogeneous glass matrix that has extremely low leach rates and, thus, is considered to be nonhazardous.

As the glass cools, devitrification may occur. Devitrification is the precipitation of crystal phases from the glass. Depending on the phases that precipitate, devitrification can adversely affect the durability of the waste form. A limited amount of devitrification is expected that would have insignificant effects on the durability of the glass.

Glass is also considered a brittle material. Rapid cooling of the glass induces stresses in the glass that can lead to fracturing. It is important to consider fracture when applying this waste form to large-scale blocks (0.3 to 0.6 m dia. x 1 to 3 m in length [1 to 2 ft dia. x 3 to 10 ft in length]). Stresses within the glass can be relieved if the glass block is allowed to cool slowly (over months). This long cooling time is not generally considered practical, due to time and equipment constraints. Thus, the glass cast into containers will contain fractures. Slow cooling can also be detrimental as it will favor devitrification.

The effect of radiation to the glass matrix is expected to be small. Chemical durability is affected by the alpha decay by a factor of ≤ 3 (Lutze and Ewing 1988).

II.2 TAILORED CERAMICS

In this context, tailored ceramic includes the work of Ringwood et al. (1980) on 'Synroc' and that of Harker et al. (1983) and Grantham et al. (1983) on tailored ceramic. When these waste forms are applied to defense waste, the formulations developed are similar because of the quantity of nepheline generated by Hanford Site waste.

A ceramic waste form is used in two treatment options, hot isostatic pressed (HIP) ceramic and ceramic pellets.

II.2.1 Formulation

Tailored ceramics were applied to the technology of consolidating HLW. The waste composition combined with chemical additives forms the tailored ceramic. The HLW would be chemically bound to the crystalline phases forming the ceramic structure. Tailored ceramics can be designed to immobilize the waste by two methods. The ceramic can be designed to contain a low loading of radionuclides by selecting appropriate phases within the ceramic, or a dilute solid solution can contain a high loading of radionuclides. This waste form has been applied to high aluminum composition HLW at the Savannah River Site.

Crystal structure and the number of phases have been identified for HLW consolidation. Table II-2 identifies possible host phases for polyphase ceramic nuclear waste

Table II-2. Host Phases for Polyphase Ceramic.

Host	Assemblage	Structure Composition
Actinide and rare earth	Fluorite structure solid solutions	$UO_2-ThO_2-ZrO_2$
	Zirconolite	$CaZrTi_2O_7$
	Pyrochlores	$(Gd,La)_2Ti_2O_7$
	Perovskites	$CaTiO_3$
	Monazite	$(Gd,La)PO_4$
	Zircon	$ZrSiO_4$
Strontium and alkaline earth	Magnetoplumbites	$(Ca,Sr)(Al,Fe)_{12}O_{19}$
	Perovskites	$(Ca,Sr)TiO_3$
	Hollandite	$BaA_{12}Ti_6O_{16}$
Alkali	Nepheline	$(Na,Cs)AlSiO_4$
	Perovskite	$(Gd,La)_{0.5}Na_{0.5}TiO_3$
	Magnetoplumbite	$(Na,Cs)_{0.5}La_{0.5}Al_{12}O_{19}$
	Hollandite	$(Ba_xCs_yNa_z)Al_2Ti_6O_{16}$
	Silica-rich amorphous intergranular phases	
Metal host phases	Alloys	Mo-Ru-Tc-Pd-Ag-Rh-Ni-Tc
Nonfission Product host phases	Spinel	$(Mg,Ni,Fe)(Al,Fe,Cr)_2O_3$
	Corundum	Al_2O_3
	Rutile	TiO_2
	Pseudobrookite	Fe_2TiO_5

form design. The host phase has the ability to chemically bind a specific waste element. Additional strength and chemical durability can be designed into the waste form when adding an excess of the tailoring species.

The ceramic form evaluated for this application is an aluminosilicate compound, Synroc D, which consists of zirconolite, perovskite, spinel, and nepheline. Sodium is immobilized in this compound as nepheline. The theoretical sodium oxide loading of nepheline is 22 wt%. The calculated waste loading based on all formulation assumptions is 78 percent and 24 percent for HIP and ceramic pellet, respectively. For the application of the Hanford Site waste, the major mineral assemblages used would be nepheline, monazite, and corundum.

Table I1-2 shows that for waste high in sodium, nepheline, or a glass phase is the required host for alkalis.

I1.2.2 Quantities Made

The amount of tailored ceramic made and placed into canisters will be determined by the separations technology combined with the ceramic process.

Table I1-3 identifies the number of canisters that would be produced using different separations treatments combined with a tailored ceramic treatment option. A larger canister could be used to produce less canisters as shown by Table I1-3.

I1.2.3 Physical Properties

Like glass, a ceramic is a very durable waste form. Waste oxides are contained in a homogeneous ceramic matrix that is considered nonhazardous.

Few leaching studies have been performed to demonstrate all dissolution kinetics for tailored ceramics. Observations identified for nepheline indicate that the silicate phase within the matrix will determine the short-term leaching behavior. The pH conditions will determine the amount of silicate that leaches from the matrix.

Ceramic is highly resistant to radiation damage. Because of the low specific activity of the Hanford Site SST wastes, radiation should have a negligible effect on the integrity of the ceramic over 10,000 years.

I1.2.3.1 Product Stability. SST waste matrixed within ceramic will be a highly stable, low dispersal waste form under expected repository conditions. Relative to other waste forms, ceramics are considered to be very leach resistant.

Table II-3. Tailored Ceramic Process Canister Production Estimates.

Process	Separations technology used	HWVP canister (0.6 m dia. x 3.17 m h)	Large canister (0.68 m dia. x 4.76 m h)	Shielded cask (2.13 m dia. x 5.79 m)
Hot isostatic pressed	Sludge wash	10,600	5,200*	
Ceramic pellet	None		230,000	29,600*

*Container size used for process evaluation.
HWVP = Hanford Waste Vitrification Plant

Ceramic is not combustible and is resistant to fire damage. Melting or softening would occur at temperatures above 800 °C (1472 °F) and volatilization occurs when temperatures exceed 1200 °C (2192 °F).

The radiation effects from short lived (<500 years) beta and gamma emitters (cesium, strontium) will mainly affect the nepheline phase. This decay can cause elevated temperatures [400 - 600 °C (752 - 1112 °F)] at the centerline of the matrix. Because of ionization and a few atomic displacements, a small fraction of the nepheline may be damaged. The damaged nepheline may be subject to recrystallization into silicate and other phases. The silicate phase could then react with water to release sodium and silicon.

The impact on the long-term chemical durability of alpha radiation damage to the crystalline phases in tailored ceramic waste forms is not completely understood. Radiation damage can occur within a phase of the ceramic matrix and results in swelling, microfracture, and local changes in the chemical bonding of effected cations. Alpha decay doses would need to exceed 10^{24} alpha decay events per cubic meter for significant damage to occur (Lutze and Ewing 1988).

Ceramic is generally a durable material. Its behavior under repository conditions for 10,000 year remains somewhat speculative; a fact that is true for all other waste forms. Indeed, current repository models do not consider the specific chemical waste form in designing systems for containment of radionuclides.

II.2.3.2 Dangerous Waste Designation. Regulations for designation of a waste form are in WAC 173-303. The regulations pertinent to designation of a SST waste form are (1) the dangerous waste characteristics, (2) dangerous waste lists and listed waste requirements, and (3) dangerous waste criteria. The dangerous waste characteristics are ignitability, corrosivity, reactivity, and TCLP toxicity.

A preliminary review of the waste form and process was completed with respect to the WAC 173-303 requirements for dangerous waste designation. This review was completed only to allow comparison of the waste forms and does not constitute a comprehensive waste designation.

Ceramic is not considered to be ignitable, corrosive, or reactive.

Because of its inherent low leachability and the constituents of ceramic, i.e., oxides, ceramic is expected to be not hazardous by the TCLP.

Some SSTs have received listed dangerous waste and thus the final form generated may be regulated as a listed dangerous waste. Under this interpretation of the regulations, the dangerous waste criteria for toxic dangerous waste appears to be the most important for the waste in these tanks.

Volatile listed waste constituents will be stripped by the feed concentration step or incinerated by the firing operation.

Ceramic is not a toxic waste by the book designation procedure.

II.3 CALCINED PRODUCTS

Calcining the waste to produce a powder waste form is in one treatment option that is identified as calcine-cask.

II.3.1 Formulation

Metal oxides, generated from the waste, will be almost 100 percent of the calcination product depending on the composition of the waste feed. With the proposed process, it is expected that some of the particles forming the inert bed in the calciner will elutriate along with the calcined product stream and will be about 10 percent of the overall output. The final waste form of the calcined product itself will be amorphous particles and/or an aggregate of very small microcrystalline particles.

Calcination has been demonstrated on feed materials containing 80 to 210 g calcine/L liquid waste (0.7 to 1.7 lb/gal). The waste contained 0.01 molar to 1 molar sodium (Bjorklund 1977). Calcination of HLW has also been performed at Idaho National Engineering Laboratory (INEL).

11.3.2 Quantities Made

The amount of calcined product made and placed into canisters will be determined by the efficiency of the fluidized bed calciner and the amount of inert bed material needed to prevent agglomeration in the calciner. Other methods of processing (e.g., plasma arc) are available, but the fluid bed was considered the best developed option. (The process, as evaluated, was presented by a representative of the Yakima Indian Nation.)

Table 11-4 identifies the number of canisters that would be produced using different size canisters. A large cask is used to produce less canisters as shown by Table 11-4.

Table 11-4. Calcine Process Canister Production Estimate.

Process	Separations technology used	HWVP canister (0.6 m dia. x 3.17 m h)	Large canister (0.68 m dia. x 4.76 m h)	Shielded cask (2.13 m dia. x 5.79 m)
Calcine-cask	None	273,000	121,000	17,700*

*Assumed container size for process.

HWVP = Hanford Waste Vitrification Plant

11.3.3 Physical Properties

The physical form of the calciner product has a number of disadvantages compared with glass and ceramics. These disadvantages are dispersibility of the powder, solubility, susceptibility to radiolytic decomposition, and corrosivity as a consequence of its high pH in solution. These points are expanded below.

Calciner product, being a fine powder, is highly dispersible and thus may not meet transportation and repository acceptance criteria. Because of this dispersibility, calcination has generally been thought of as being an intermediate stage in a process that would ultimately produce a more inert product for disposal. Enrobing in an inert matrix would achieve this end. Such a matrix could be metal, glass, or ceramic.

Calcined oxides with a high alkali metal content are hygroscopic and readily dissolve in water. Calcined tank waste is generally high in sodium content and, when combined with moisture, forms a high pH solution, which is corrosive.

Test data on the leachability of INEL calcine product has indicated that 60 percent of the ^{137}Cs and 40 percent of the ^{90}Sr was removed after 2,000 hours of continuous leaching with water at 25 °C (77 °F). Other oxide calcines exhibit comparable leach rates (NAS 1979).

Calcination reactions may not go fully to completion to the extent that glass reactions do because of lower operating temperature. Temperatures above 600 °C (1112 °F) result in degradation. Should the calcine product be heated above 600 °C (1112 °F), volatilization of some radionuclides and decomposition of some chemicals would occur.

11.3.3.1 Dangerous Waste Designation. Regulations for designation of a waste form are in WAC 173-303. The regulations most pertinent to designation of a SST waste form are (1) dangerous waste characteristics, (2) dangerous waste lists and listed waste requirements, and (3) dangerous waste criteria. The dangerous waste characteristics are ignitability, corrosivity, reactivity, and TCLP toxicity. Some of the Hanford Site waste tanks have received listed dangerous waste and thus the final form, after treatment for disposal, may be regulated as a listed dangerous waste. With respect to these tanks, the dangerous waste criteria for toxic dangerous waste appears to be the most important.

A preliminary review of the waste form and process was completed with respect to the WAC 173-303 requirements for dangerous waste designation. This review is intended to allow comparison of the different waste forms and does not constitute a comprehensive waste designation.

Calcined waste does not meet the definition of an ignitable material.

Water is expected to react with the calcine and form a corrosive solution with high pH.

Results of the U.S Environmental Protection Agency TCLP test on the calcine product are unknown at this time. Compared to other waste forms, the calcine product is not considered to be leach resistant. This waste form would not provide the required structural stability in the presence of moisture and therefore would rely entirely on the container to meet the requirements in 10 CFR 61.56(b)(1) for land disposal.

Volatile listed waste constituents will be generated as the result of radiolytic decomposition of the calcine product.

The designation of the waste that results from the book designation procedure for toxic dangerous waste will depend on the extent to which calcination destroys nitrite present in the waste. If less than 99.9 percent of the nitrite is destroyed, the calcined product will be extremely hazardous waste. If nitrite destruction is better than 99.9 percent but less than 99.99 percent, calcination leaves a dangerous waste. If nitrite destruction exceeds 99.99 percent, the calcined product is not a toxic waste.

11.4 TECHNOLOGY OPTIONS NOT EVALUATED

This section comments on those technology options/waste forms that were not evaluated in the study.

11.4.1 Concretes

Concretes were not considered for detailed analysis in this study. In general, waste form volume is more than double that of other, better waste forms (e.g., glass). This is reflective of the actual waste loading in the waste form. Other reasons for not studying further concrete-based waste forms are loss of durability when exposed to high temperature, a higher leach rate than other waste forms, and noncompatibility with high sodium nitrate waste resulting in a poor product.

A brief description of specific individual concrete systems follows.

11.4.1.1 FUETAP Concrete. FUETAP is an acronym for 'formed under elevated temperature and pressure.' This process uses accelerated curing to produce strong, durable, and relatively impermeable solids. FUETAP generally consists of portland cement, non-portland hydraulic cement, fly ash, sand, clays, and waste products.

Initial tests were applied to a high sodium nitrate concentration waste. When combinations of portland cements and waste were used, curing at experimental temperatures and pressures produced a waste form from which small amounts of a sticky nitrate substance exuded. The durability was such that the pellets cracked easily after this (Schulz et al. 1980).

Waste loading cannot exceed 15 wt% when applied to high sodium nitrate wastes such as those at the Hanford Site.

11.4.1.2 SupergROUT Concrete. SupergROUT is a term used to describe a grout consisting of the Hanford Site liquid radioactive waste, cement, and special additives to decrease radionuclide leachability and improve other properties of the final concrete.

Waste oxide loadings of the Hanford Site blended waste and residual liquid immobilized in this waste form are estimated to be 13 and 18 wt%, respectively with waste densities of 0.18 and 0.24 g/cm³. The leach rates for the grout product are 10⁻⁵ to 10⁻⁷ g/cm² day for cesium and strontium.

11.4.1.3 Sludge in Concrete. This waste form is a concrete monolith similar to grout that immobilizes waste-insoluble sludges. Processing occurs at ambient temperatures and pressures.

The expected waste loading range of this waste form for a typical waste oxide loading is between 5 wt% and 19 wt% (Schulz et al. 1980).

II.4.2 Miscellaneous

The waste forms classified as miscellaneous are relatively different from each other in composition. The link between them would be that the waste form loading and leach rates would be low compared to other, superior waste forms identified.

II.4.2.1 Bitumen. The waste form consists of radioactive waste and an asphalt matrix. Processing can be done at relatively low operating temperatures because the bitumen has a low softening temperature of around 100 °C (212 °F).

A temperature limit of 50 °C (122 °F) is proposed for a thermal stability requirement to minimize long-term (1,000 years) settling of waste particles (Kluger et al. 1979). The repository with a design peak temperature of 200 °C (392 °F) would exceed the thermal stability of the bitumen waste form (Ross 1992).

II.4.2.2 Aqueous Silicate. This waste form incorporates an alkaline radioactive waste and a clay to form stable aluminosilicate minerals.

The leachability of this waste form exceeds that of other waste forms. The literature reports cesium leach rates ranging from 3×10^{-2} to 3×10^{-4} g/cm²·day. Immersion in water causes the waste form to crack and swell.

The waste loading of material produced by the aqueous silicate process is low. Reports in the literature indicate that the liquid waste loading is approximately 20 wt% waste oxides and that the loading for salt cake is approximately 5 wt% waste oxides (Schulz et al. 1980).

II.4.3 Glass

Borosilicate glass is the best developed approved technology. Borosilicate glass is acceptable to the Hanford Site waste. A high silica glass product would produce more waste because of the waste loading. Glass ceramics require complex processing equipment and facilities.

II.4.3.1 Porous Glass Matrix. This waste form is a high silica glass that incorporates the radioactive waste by sintering porous glass frit and waste. The process operating temperature of 900 to 1100 °C (1650 to 2000 °F) is lower than that in a conventional glass melter. The high silica waste form produces a high durability glass. However, when combined with high sodium waste, the durability is the same as for a borosilicate glass.

The waste loading would be limited to 20 wt%.

II.4.3.2 Glass Ceramics Monoliths/Marbles. The glass ceramic process produces a glass that is then heat treated to nucleate and grow a fine crystalline microstructure. This waste

form is chemically and structurally more durable than other glass waste forms. Developing and providing an initial waste feed composition to grow the ceramic would be complex and the wide variation in composition of the Hanford Site wastes would delay development of the several different compositions needed to successfully produce this waste form.

11.4.4 Ceramics

See Section 11.2 for details on tailored ceramics.

11.4.5 Multilayer Waste Forms

These waste forms normally have two layers. The first layer is typically a glass or ceramic and the second layer is a matrix covering the prime form. The discussion will center around the second layer, because glass and ceramic waste forms are discussed in detail in Sections 11.1 and 11.2, respectively. In general, little or no advantage is gained by these forms over uncoated glass and ceramic wastes that already adequately meet requirements.

11.4.5.1 Cement Matrix. For the waste form to be thermally stable, the temperature should not exceed 300 °C (572 °F). High pH solutions, which are present in cement matrices, react with glass and ceramics and so such mixtures are likely to have higher leach rates. No leach rate data are currently available.

The waste loading is lower than the uncoated waste form and does not exceed 18 wt% on an oxide basis.

11.4.5.2 Coated Ceramic. Waste loadings have not been determined for the coated ceramic. It is assumed that the waste loading will be less than the monolithic tailored ceramic waste form.

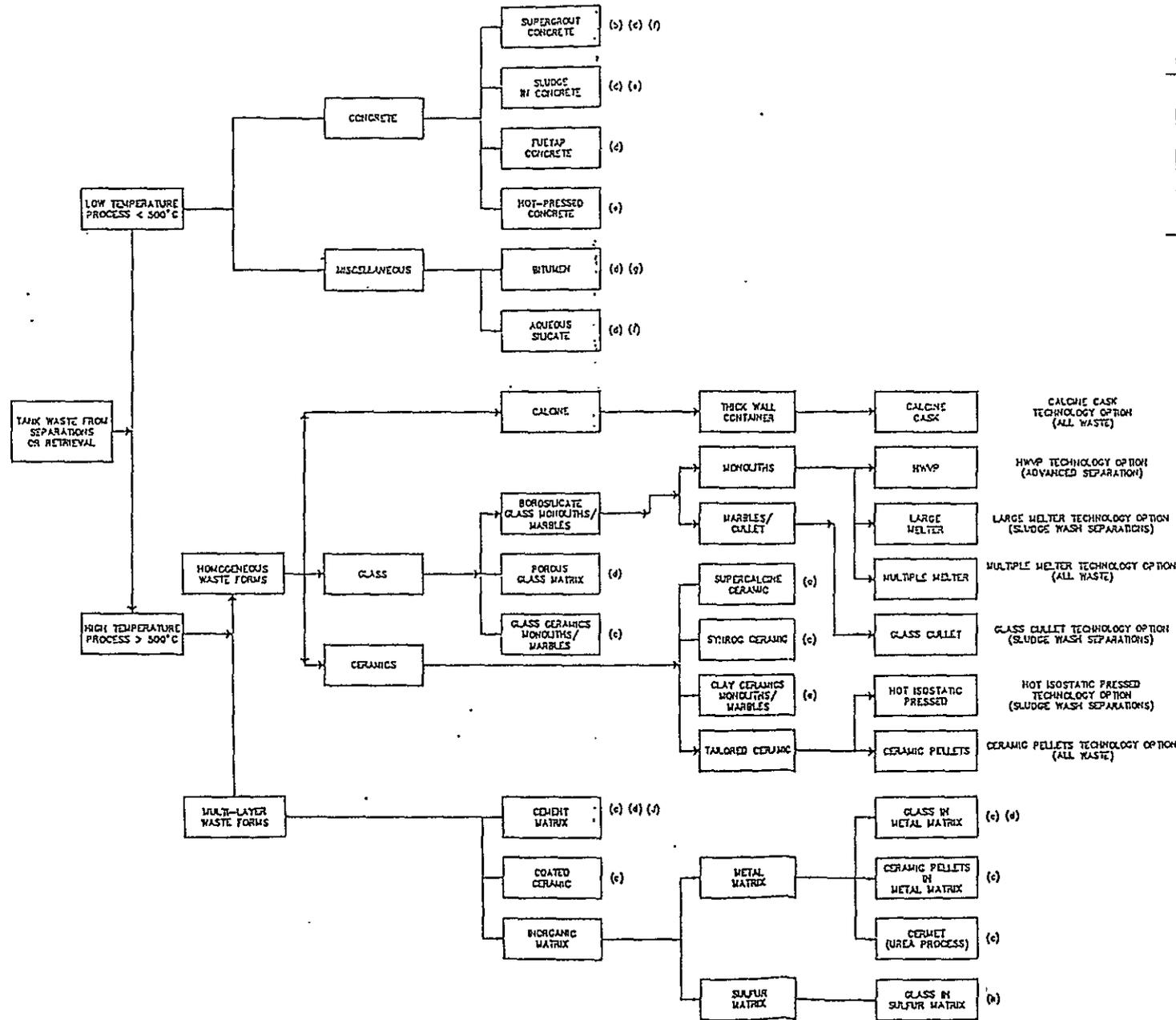
11.4.5.3 Metal Matrix. The metal matrix would be approximately 50 percent of that for monoliths. This would increase the volume of the waste form significantly.

11.4.5.4 Inorganic Matrix. The matrix in this case was polymerized sulfur. Currently, the sulfur matrix is not acceptable at the repository. Only borosilicate glass has been approved as a waste form in the repository. The sulfur matrix would need additional compatibility testing to be performed with the Hanford Site waste.

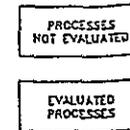
11.3.1.1 Product Stability. Vitriified single-shell tank (SST) waste will be a highly stable, low dispersal waste form. Glasses are considered to be very leach resistant. Glass is less leach resistant than ceramics but is significantly better than calcines or grout.

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Figure 11-1. Offsite Disposal Technology Option.



LEGEND



NOTES

- (a). PROCESS AND WASTE FORM SIMILAR TO TAILORED CERAMIC.
- (b). BULK PROCESS NOT APPLICABLE TO CONTAINERIZED FORMS.
- (c). PROCESS COMPLEXITY HIGH.
- (d). WASTE FORM VOLUME MORE THAN TWICE THAT OF GLASS MONOLITHS.
- (e). PROCESS LIMITED TO LOW SODIUM WASTE. PROCESS IS LOW PRIORITY ALTERNATIVE TO VITRIFICATION AT HWMP.
- (f). LEACHABILITY EXCEEDS BOROFLUORATE GLASS 100X.
- (g). SUSCEPTIBLE TO DEGRADATION AT REPOSITORY TEMPERATURE.
- (h). REPOSITORY ACCEPTANCE UNCERTAIN.
- (i). GLASS SUSCEPTIBLE TO CORROSION AT HIGH pH OF CEMENT.

Glass is highly resistant to radiation damage. Because of the low specific activity of the Hanford Site SST wastes, radiation should have negligible effect on the integrity of the glass over 10,000 years.

Glass is not combustible and is resistant to fire damage. Melting or softening would occur at temperatures above 800 °C (1472 °F) and volatilization occurs when temperatures exceed 1200 °C (2192 °F).

Glass is generally a durable material. However, it may not survive under repository conditions for 10,000 years. Currently, repository models do not consider the waste form for containment of radionuclides.

II.3.1.2 Dangerous Waste Designation. Regulations for designation of a waste form are in *Washington (State) Administrative Code (WAC) 173-303 "Dangerous Waste Regulations"*. The regulations most pertinent to the designation of a SST waste form are (1) the dangerous waste characteristics, (2) dangerous waste lists and listed waste requirements, and (3) dangerous waste criteria. The dangerous waste characteristics are ignitability, corrosivity, reactivity, and toxicity characteristic leaching procedure (TCLP) toxicity. At least some SSTs have received listed dangerous waste, and thus the final form may be regulated as a listed dangerous waste. With respect to SST waste, the dangerous waste criteria for toxic dangerous waste appears to be the most important.

A preliminary review of the waste form and process was completed with respect to the WAC 173-303 requirements for dangerous waste designation. This review allowed comparison of the waste forms and does not constitute a comprehensive waste designation.

Glass is not considered to be ignitable, corrosive, or reactive.

The constituents of glass, i.e., oxides, are either nontoxic or low toxicity chemicals by the book designation procedure. Because of its inherently low leachability, and the constituents of glass being oxides, glass is expected to be not hazardous by the TCLP toxicity characteristic.

Volatile listed waste constituents will be stripped by the feed concentration step or incinerated by the melter operation.

Glass is not a toxic waste by the book designation procedure.

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