EGG-WTD--10058

DE92 018049

Thermal Processing System Concepts and Considerations for RWMC Buried Waste

**T. L. Eddy
P. C. Kong
B. D. Raivo
G. L. Anderson**

Published February 1992

**Idaho National Engineering Laboratory
EG&G Idaho, Inc.
Idaho Falls, Idaho 83415**

**Prepared for the
U.S. Department of Energy
Office of Environmental Restoration and Waste Management
Under DOE Idaho Field Office
Contract DE-AC07-76ID01570**

MASTER

DISTRIBUTION OF THIS DOCUMENT IS UNLIMITED

Thermal Processing System Concepts and Considerations for RWMC Buried Waste

EGG-WTD-10058

Prepared by:

Peter C. Kong 3-27-92
P. C. Kong Date

Thomas L. Eddy 3/27/92
T. L. Eddy Date

Brian D. Raivo 3-27-92
B. D. Raivo Date

Reviewed by:

A. Donaldson 3/27/92
A. Donaldson Date

J. R. Weidner 3/27/92
J. R. Weidner Date

S. O. Bates 3/27/92
S. O. Bates Date

Reviewed and Approved by:

G. L. Anderson 3/24/92
G. L. Anderson Date

D. E. Shropshire 3/30/92
D. E. Shropshire Date

ABSTRACT

This report presents a preliminary determination of ex situ thermal processing system concepts and related processing considerations for application to remediation of transuranic (TRU)-contaminated buried wastes (TRUW) at the Radioactive Waste Management Complex (RWMC) of the Idaho National Engineering Laboratory (INEL). Beginning with top-level thermal treatment concepts and requirements identified in a previous Preliminary Systems Design Study (SDS), a more detailed consideration of the waste materials thermal processing problem is provided. Anticipated waste stream elements and problem characteristics are identified and considered. Final waste form performance criteria, requirements, and options are examined within the context of providing a high-integrity, low-leachability glass/ceramic, final waste form material. Thermal processing conditions required and capability of key systems components (equipment) to provide these material process conditions are considered. Information from closely related companion study reports on melter technology development needs assessment and INEL Iron-Enriched Basalt (IEB) research are considered. Five potentially practicable thermal process system design configuration concepts are defined and compared. A scenario for thermal processing of a mixed waste and soils stream with essentially no complex presorting and using a series process of incineration and high temperature melting is recommended. Recommendations for applied research and development necessary to further detail and demonstrate the final waste form, required thermal processes, and melter process equipment are provided.

FOREWORD

This report was prepared for the Waste Technology Development Department of EG&G Idaho, Inc., under contract to the U. S. Department of Energy Office of Technology Development Idaho Field Office. Funding was provided under FY-91 Thermal Processing Technologies Technical Task Plan ID-0502-DT, 1991, and ID-040E-2D, 1992.

This is one of a series of reports prepared for the Thermal Processing Technologies Project. Two other closely related reports in the series present a "Melter Development Needs Assessment," and "A Survey of INEL Research on the Iron-Enriched Basalt Waste Form."

Contributions to the report far exceed the list of authors and reviewers. We appreciate the assistance of all those who contributed to this effort.

CONTENTS

ABSTRACT	iii
FOREWORD	v
ACRONYMS	xiii
EXECUTIVE SUMMARY	xv
1. INTRODUCTION	1
1.1 Background	1
1.2 Overview	2
2. CLASSIFICATION OF INPUT WASTE STREAMS	4
2.1 As-Found Classification	4
2.1.1 Basis for the As-Found Classification	4
2.1.2 Initial As-Found Classification	6
2.1.3 Proposed As-Found Classification	6
2.1.4 Potential As-Found Process Considerations	10
2.1.5 Volume Reduction Considerations	10
2.2 As-Separated Classification	13
2.2.1 Basis for the As-Separated Classification	13
2.2.2 Initial As-Separated Classification	14
2.2.3 Potential As-Separated Process Considerations	14
2.3 Recommended Classification of Waste Streams	18
3. CRITERIA AND REQUIREMENTS FOR FINAL WASTE FORM	21
3.1 Summary	21
3.2 Nuclear Final Waste Form Development	22
3.2.1 Borosilicate Glass (BSG)	24
3.2.2 High Alumina-Silicate Glasses	28
3.2.3 Iron-Enriched Basalt (IEB)	28
3.2.4 Glass-Ceramics	30
3.2.5 Phosphate Glasses	30
3.2.6 Synroc	32
3.2.7 Recommendations	32

3.3	Criteria for RWMC TRU Final Waste Form	33
3.3.1	System Design Study Generalized Criteria	33
3.3.2	Desirable Final Waste Form Characteristics and Criteria	33
3.4	Final Waste Form Evaluation	34
3.4.1	Materials Characterization Methods	34
3.4.2	Sampling and Bulk Characterization	35
3.4.3	Chemical, Phase, and Morphological Analyses	35
3.4.4	Chemical Durability	35
3.4.5	Physical Durability	36
3.4.6	Radiation Durability	36
3.4.7	Proposed Waste Form Characterization Methods for Tests	37
4.	WASTE STREAM PROCESSING	39
4.1	Introduction	39
4.2	Systems Design Scenarios	39
4.2.1	General Considerations	39
4.2.2	The SDS Scenario	42
4.2.3	The Simple Retrieval and Burden Soil Separation Scenario	49
4.2.4	The SDS Retrieval and Total Soil Separation Scenario	56
4.2.5	The SDS Retrieval and Soils Processing Scenario	56
4.2.6	The Borosilicate Glass Scenario	61
4.2.7	Comparison of Scenarios and Options and Recommendations	61
4.3	Radiological Assays	63
4.4	Processes in the Melter	65
4.4.1	Physical Processes in the Melter	65
4.4.2	Chemical Processes in the Melter	66
4.4.3	Vitrification/Devitrification Processes in Slag	69
4.5	R&D to Optimize the Waste Form and Processes	69
4.5.1	Recommended R&D and Priorities	70
4.5.2	Proposed Testing	71
4.5.3	Potential Collaborators to Solve Problems	72
5.	FIRST TEST SERIES RESULTS	74
5.1	Review of the First Test Series	74
5.2	Melter Shakedown Tests	74
5.3	Scientific Experiments	75

6.	CONCLUSIONS AND RECOMMENDATIONS	78
6.1	Input Waste Streams	78
6.2	Final Waste Forms	78
6.3	Processing Systems	78
6.4	Recommended R&D	79
7.	REFERENCES	80
	Appendix A—Source Data for Waste Streams and Scenarios	A-1
	Appendix B—Materials Characterization Methods	B-1

FIGURES

S-1.	A conceptual, not-to scale incineration and melting system with no sorting (other than Special Case)	xvi
S-2.	An approximate mass flow diagram of input waste streams and output waste forms based on estimated values	xx
S-3.	Relative mass (left) and volume (right) fractions of the TRUW, entrained soil, underburden soil and overburden soil for Pit 9. Areas are similar because mean specific gravities are approximately two	xxii
S-4.	Scenario II-E, the most highly recommended incineration and melting system scenario	xxvi
S-5.	Illustration of the effect of adding flux to the slag melt	xxix
2-1.	A schematic overview of the major storage activities at RWMC related to this work	5
2-2.	Relative mass fractions of material categories of Pit 9	9
2-3.	Component waste streams for As-Separated classification based on the Presort Option in Figure A-1	15
2-4.	Preliminary process flow diagram of material categories within waste streams to indicate the probable types of processing needed	17
3-1.	Historical development of the nuclear final waste forms	25
3-2.	Tolerance range of major oxides in IFB	31
4-1.	Scenario I - SDS process incineration and melting system with LLW pre or post sort	43

4-2	Conceptual sketch of electrically-heated melters: (a) Joule-heated melter with the immersed electrodes in the horizontal configuration, (b) an arc-heated melter with 3-phase AC operation and graphite electrodes, and (c) a plasma-heated melter with 1-phase DC operation and both electrodes in the torch	44
4-3.	The INEL Joule-heated melter with molybdenum electrodes used for IEB research	45
4-4.	Plasma-heated melter torch-electrode configurations: (a) transferred-arc torch with the melt as the cathode and (b) nontransferred-arc torch with both electrodes in the torch	46
4-5.	Plasma-heated melter used in the INEL PAFE experiment in the transferred-arc mode with 1-phase DC operation, metal electrode torch, an oxygen lance, and water-cooled skull with a rotating chamber that is slowed to pour the slag	47
4-6.	Scenario II-A - Combined Incineration and Melting System with Simple Retrieval and over/under burden soil separation from the treated waste stream. Option A - no sorting other than Special Case	50
4-7.	Scenario II-B - Separated Incineration and Melting System with Simple Retrieval and over/under burden soil separation. Option B - Sorting combustibles only	53
4-8.	Scenario II-C - Separated Incineration and Melting System with Simple Retrieval and over/under burden soil separation. Option C - Sorting combustibles, noncombustibles (including entrained soil), and metals.	54
4-9.	Scenario II-D - Separated Incineration and Melting System with Simple Retrieval and over/under burden soil separation. Option D - Sorting metals only	55
4-10.	Scenario II-E - Separated Incineration and Melting System with Simple Retrieval and over/under burden soil separation. Option E - No sorting other than Special Case. Also includes the air-plant and zero-emissions options.	57
4-11.	Scenario III - Scenario II options but including the SDS Retrieval Subsystem and total soil separation.	59
4-12.	Scenario IV - Scenario II options but including the SDS Retrieval Subsystem, total soil separation, and the SDS Soil Processing Subsystem.	60
4-13.	Scenario V - Scenario II options but including the SDS Retrieval Subsystem, total soil separation, SDS Soil Processing Subsystem, and with a Borosilicate Glass final waste form.	62
4-14.	Types of and requirements for radiological assays at various stages in the generic processing scenario	64

5-1.	Microphotographs of the slag waste form from the PEC, ACT, and RWMC tests (1000X). The PEC slag is predominantly amorphous glass. The RWMC slag is predominantly crystalline rock	77
------	---	----

TABLES

S-1.	Material categories identified and estimated quantities in each of the major waste streams	xviii
S-2.	A qualitative comparison of the properties of various glasses and glass-ceramics	xxiii
S-3.	Processing options for using various Joule-heated and plasma-heated melters to make different viable waste forms	xxx
2-1.	Preliminary tabulation of materials found in buried waste in selected trenches and pits	7
2-2.	Proposed As-Found classification of input waste streams. Mass/Volume data is from Pit 9 with estimated conversions from A-10	8
2-3.	Expected potential problems and possible fixes for the various material categories of the input waste streams. Note that all substances may have radiation-hazard problems. Most of the reactive materials and radionuclides should be in the oxide state	11
2-4.	Various volumes and calculated volume reduction or compaction ratios for Pit 9 based on estimated volumes and masses	12
2-5.	Initial As-Separated classification of input waste streams. Mass/Mole data is for Pit 9 as estimated from Tables A-10 and A-11. Pit 9 has no record of LLW from the INEL. The basis for the molecular weight is given in parenthesis.	16
2-6.	Recommended As-Separated classification of input waste streams	20
3-1.	Desirable final waste form characteristics	23
3-2.	Desirable process considerations for waste form development	23
3-3.	Typical range of waste glass composition	26
3-4.	Characteristics of different waste forms compared to BSG	27
3-5.	Cation size indices and valency for ionic exchange reaction	29
3-6.	Summary table of chemical, irradiation, and mechanical durability tests for the final waste forms	38

4-1. Summary of the options included in the system design scenarios	40
4-2. Comparison of input sorting Options A, B, C, D & E	58
4-3. Potential researchers and collaborators to solve problems	73

ACRONYMS

ACT	afterburn component test
BSG	borosilicate glass
CDIF	Component Development Integration Facility
CERCLA	Comprehensive Environmental Response, Compensation, and Liability Act
CFR	Code of Federal Regulations
DOE	Department of Energy
DOT	Department of Transportation
EAF	electric arc furnace
EPA	Environmental Protection Agency
HLW	high-level waste
HVPM	high vapor-pressure metals
IEB	iron-enriched basalt
INEL	Idaho National Engineering Laboratory
ISV	in situ vitrification
JHM	Joule-heated melter
LDR	land disposal restrictions
LL	low-level radionuclides
LLW	low-level waste
MAP	mixed activation product
MFP	mixed fission product
MSDS	material safety data sheet
NRTS	National Reactor Testing Station
PAFE	plasma arc furnace experiment
PCR	plasma centrifugal reactor
PHM	plasma-heated melter
PNL	Pacific Northwest Laboratory
R&D	research and development
RCRA	Resource Conservation and Recovery Act
RFP	Rocky Flats Plant
RWMC	Radioactive Waste Management Complex
SDA	Subsurface Disposal Area
SDS	Preliminary System Design Study Report (Ref 1)
SRL	Savannah River Laboratory
TPI	thermal processing technologies
TRA	Test Reactor Area
TRAMPAC	DOT nuclear waste transportation requirements
TRU	transuranic
TRUW	transuranic-contaminated waste
ISA	Transuranic Storage Area
USBM	U.S. Bureau of Mines
USGS	U.S. Geological Survey
WIPP	Waste Isolation Pilot Plant
WM	Waste Management Department
WTDD	Waste Technology Development Department
WSEP	Waste Solidification Engineering Prototypes

EXECUTIVE SUMMARY

Introduction

Beginning with results from existing preliminary systems design studies (SDS), the work reported here provides the next level of preliminary conceptual design determination for thermal treatment-based processing of Idaho National Engineering Laboratory (INEL) buried wastes. Transuranic (TRU)-contaminated buried wastes at the Radioactive Waste Management Complex (RWMC) Subsurface Disposal Area (SDA) require remediation via the Comprehensive Environmental Response, Compensation, and Liability Act (CERCLA) decision process in order to remove the INEL from the National Priorities List (NPL) of the Environmental Protection Agency (EPA). The buried wastes and contaminated soils represent a highly heterogeneous mixture of combustibles and noncombustibles contaminated with Resource Conservation and Recovery Act (RCRA)-listed and characteristic hazardous materials and TRU radionuclides. Based upon the system design studies, proposed thermal processing concepts involve incineration for combustion elimination of hazardous organics and melting/vitrification for stabilization of the hazardous noncombustibles and TRU elements as a long-lived glass ceramic final waste form.

In particular, this study focuses on a determination of the melting/vitrification process conditions and enabling technologies within the context of developing a total thermal systems application to the RWMC buried wastes. Development of a processing system requires determination of the incoming waste materials to be processed, determination of the output product material performance required, and an iterative design match of available and improved process systems technology components (equipment) capabilities to the desired process parameters.

As an example, a conceptual incineration and melting system with no sorting (other than a bulk presort of Special Case waste items) is illustrated in Figure S-1 and is briefly described in the following. A simplified retrieval system is located in a temporary alpha containment building located over the pit to be excavated. An overhead crane is available to relocate oversized or highly radioactive items. The manually-operated backhoe is shielded and is used for loading drums, containers, and soil into sealable bins on conveyor belts. The bins are sealed, assayed for content, and transported to the processing building where they are routed into the appropriate order or feed line to be emptied into the sizing unit.

The entire thermal processing system from the sizing unit on through the offgas treatment system exhaust and the waste form packaging unit is enclosed for alpha containment. After sizing, the unsorted waste goes through a thermal desorption process to initiate decomposition of volatile organics at low temperature, then to the incinerator to initiate combustion/pyrolysis and to preheat noncombustible solids in the waste stream. The gaseous products of incomplete combustion from the incinerator are routed to an afterburner to ensure complete combustion of hydrocarbons (the afterburner provides residence time and temperature to ensure complete destruction of dioxins and other potential intermediate toxic hydrocarbons). Offgases from the melter also go to the afterburner. The offgas treatment system removes any volatilized metals and metal oxides, halogen and sulfur compounds, (acid gases) and other precipitable compounds. These will be later treated as a secondary waste stream, as necessary. The exhaust gases to the atmosphere are clean carbon dioxide, water vapor, and nitrogen that meet EPA and State air pollution requirements.

The noncombustible solids from the incinerator are fed into the melter by a screw conveyor in a semicontinuous mode with periods of 10 to 30 minutes. The solids temperature out of the

N92 0026

Figure S-1. A conceptual, not-to scale incineration and melting system with no sorting (other than Special Case).

incinerator/pyrolyzer must be controlled to minimize agglomeration and corrosion in the screw conveyor. In the melter, the new solids (feed burden) are anticipated to form a cold cap over the slag melt which may help to inhibit loss of the high vapor pressure metals and their oxides. The middle layer in the melter is the molten slag composed of silica and metallic oxides that will yield the final waste form elemental composition. The lower layer is a molten metal layer decontaminated of TRU and low-level waste (LLW) nuclides (heavy metal oxides are retained in the slag). Natural convection currents in the slag promote mixing for the desired reactions and homogeneity. The melter configuration shown is a 3-phase, AC graphite electrode submerged-arc melter. Other types and configurations of melters are possible (DC arc, plasma torch, etc.). Periodically, e.g., every 10 to 30 minutes, a barrel of liquid metal (mostly iron) is tapped and packaged for LLW disposal or possible reclamation depending upon activity level. At similar periods, one or more barrels of slag are tapped, packaged, cooled under a controlled schedule to form the desired glass/ceramic, assayed, and routed to the appropriate TRUW, reclassified LLW, or LLW temporary storage prior to permanent disposal. Melter operating procedures would generally follow those which have been in practice in the scrap melting and smelting industry for decades, with modification to ensure alpha control.

The scenario described is provided as a representative example at this point, intended to give the reader some understanding of an overall thermal processing system approach. The following sections summarize the waste stream, final waste form, and thermal processing scenario considerations.

The Input Waste Stream

Buried waste materials have been examined in this study from the standpoint of representing potential input waste streams for thermal processing. This has included determining what type and amount of materials are likely to be processed, which materials may constitute potential problems, possible process problem resolutions, whether sorting is needed or advantageous, and how these factors affect melter design and internal processing.

Existing information on SDA waste and contaminated soils was examined to identify probable input material streams for thermal processing. Two preliminary design-based waste stream classifications have been defined for subsequent thermal processing considerations in this study. An "As Found" waste stream classification is established which essentially represents a mix of all the waste materials present to be processed without separation; while an "As Separated" waste stream classification groups the wastes into separate waste streams for processing (combustibles, noncombustibles, and bulk metals). Contaminated soils are considered as a separate input material category to be processed along with the wastes.

The TRUW is buried in Trenches 1-10 and Pits 1-6 9 and 10 of the SDA at RWMC. Detailed information is available for Pit 9, with other pits and trenches expected to have similar types of materials. Major input waste streams defined for processing in the SDS were metals, combustibles, noncombustibles, and soils. Table S-1 lists the material categories identified and provides estimated quantities for each of these major streams based upon available data. Special case wastes (oversized objects, compressed gas cylinders, highly radioactive wastes, etc.) are to be separated out prior to thermal processing and treated separately. All remaining waste is to be sized by crushing, shredding, cryogenic fracture, or equivalent to approximately 2-in. dimensions.

Table S-1. Material categories identified and estimated quantities in each of the major waste streams.

<u>Material Category</u>	<u>Specified Mass or Volume</u>	<u>Calculated Estimate</u>	
		<u>Mass (kg)</u>	<u>Volume (m³)</u>
<u>TRUW Combustibles</u>			
Na, NaK, Mg (NaK)	3,469 kg	3,469	1.9
Pb, Zn (Pb in Pit 9)	7,033 kg	7,033	0.62
Hg, Li (Li in Pit 9)	238 gal	478	0.91
Hydrated oxide sludge (Al ₂ O ₃ ·H ₂ O+Fe ₂ O ₃ ·H ₂ O)	16,075 gal	65,662	61
Na/K nitrate sludge	30,149 gal	252,678	114
NaOH	859 gal	6,948	3.3
Acids (HCl, HF)	1,255 gal	4,728	4.8
Cemented organics (Portland cement only)	4,182 gal	16,694	15.8
Miscellaneous organics (incl. #12, assm'd CCl ₄)	18,724 gal	20,172	71
Organics in Ca silicate sludge (75CaSiO ₃ +25C ₂ H ₆ O ₂)	85,535 gal	1,086,781	362
Halogen Salts	0	0	0
Animal remains	0	0	0
Butyl stearate	0	0	0
Phenyls	0	0	0
<u>TRUW Non-Combustibles</u>			
Const. bricks, concrete asbestos (CaSiO ₃)	87,467 kg	87,467	83
<u>TRUW Metal Waste</u>			
Machinery, construction metals, steel drums (Fe)	658,622 kg	658,622	428
<u>LLW Materials</u>			
TRU (Pu-239)	17 kg	17	0.00085
LLW (U-238)	11,700 kg	11,700	0.59
<u>Soils</u>			
(SiO ₂ ·FeO·Al ₂ O ₃ ·CaO)			
Entrained Soil (Assumed TRU-contaminated)	191,726 ft ³	10,876,093	9,696
Underburden Soil (Assumed LLW-contaminated)	149,807 ft ³	8,498,143	4,242
Overburden Soil (Assumed Clean)	256,812 ft ³	14,568,244	7,272

For the "As Separated" case, consistent with the System Design Study (SDS), combustibles are to be routed to an incinerator with the noncombustible solid residues (ash) then routed to the melter. The contaminated soils waste stream is assumed processed by the SDS Soils Processing Subsystem, or equivalent, to separate clean, low-level, and TRU-contaminated soils, with at least the TRU-contaminated soil routed to the melter. The metals waste stream may be routed through the SDS Metals Decontamination Subsystem, or routed to the primary melter/vitrifier to be surface oxidized or decontaminated by melting in the high-temperature (1500-1800°C) oxidizing melter (iron melts at 1538°C). Any remaining melted metal could be tapped and packaged as LLW (or clean material depending upon activity level).

When mixed with soil, most of the organics, acids, bases, and reactive metals are buffered and not expected to represent significant thermal processing problems. In the melter environment, complex chemical compounds will be decomposed into oxides in the slag or produce pyrolyzed gases. Some compounds (nitrates, cemented organics, hydrated oxides, etc.) in large quantities could lead to rapid gas generation in the melter and should be sized and thermally decomposed before entering the melter. In particular, the nitrates are strong oxidizing agents, are very reactive at higher temperatures, and would be best roasted at modest temperature to convert to Na/K oxides and NO_2 . Noncemented organics and toxic materials should be mixed with soil, combusted, and the ash vitrified. High vapor pressure (volatile) metals (HVPs) such as Pb, Zn, Hg, Cs-137, etc., are expected to be oxidized and returned to some extent to the slag with transported metal vapors collected downstream in the offgas system for later treatment, e.g., vitrify at lower temperature. The exhaust gases to atmosphere would be air, water vapor, and carbon dioxide meeting EPA and State requirements.

It will probably be difficult to accurately and thoroughly identify the contents of the various incoming barrels, so a more appropriate process solution may be to combine all waste materials with sufficient soil to yield an oxidizing, fuel-laden soil which can be processed in a rotary kiln or equivalent incinerator. The noncombustible residue, preheated by its own energy source, goes to the melter. All TRU and low-level (LL) radioactive materials will be oxidized and dissolved in the slag and almost all is expected to be retained in the slag. The extent of volatilization of any TRU/LL materials will be process dependent and needs to be addressed experimentally to ensure expected retention in the slag. Available assaying technology and procedures are assumed to be adequate for safety and material process control purposes. Some application development in this area may be needed.

Figure S-2 shows an approximate mass flow input-output diagram based on estimated input waste stream quantities and assumed compositions for the non-sorted As Found case. Though approximate, it gives a rough idea of the relative amounts of different waste materials to be processed. The bulk of the waste stream is calcium silicate containing organics (25%), sodium and potassium nitrates, and metals (mostly steel not including the drums). The oxygen required to combust the organics is relatively large because of the low atomic weights of C and H. The amount of oxygen required for oxidation of the metal has been reduced from the theoretical total by assuming 30% of the metal is oversize and sorted out, 55% is tapped as pure reduced melted metal, and only the remaining 15% is surface oxidized to remove contaminants. The exhaust gas effluent volume that will result is approximately 1000 times smaller than that from a boiler in a typical electric power plant. In this "average" composition scenario, no soil is added. If soil is added, the final waste form mass will increase by the amount of soil added. Soil would be added to provide problem-material buffering and to account for variations in the no-sort composition. It is also expected that entrained soil may be difficult to separate from the wastes.

N92 0025

Figure S-2. An approximate mass flow diagram of input waste streams and output waste forms based on estimated values.

It should be noted that the potentially contaminated soil input stream to be thermally processed is from three to nine times that of the mass or volume of the buried wastes, as shown in Figure S-3. The estimated waste and soil volumes have been used to estimate the potential waste volume reduction resulting from vitrification. The compaction ratio for the waste stream, excluding soil, is about 4/1. If the net soil entrained among the containers is added to the waste, the compaction ratio is almost 3/1. Using only soil (processing only soil and no waste) would produce a reduction ratio of about 1.6/1. Heterogeneity in as-retrieved waste stream composition in a no-sort scenario will likely vary the soil fraction from 0-60%, in which case the mass of entrained soil would be more than adequate to provide for buffering in the process and produce the desired final waste form for a wide range of input waste composition. The resulting total compaction ratios should then be between 2/1 and 3/1.

The Final Waste Form

Based upon the preliminary SDS, the preferred final waste form is a highly leach-resistant, glass/ceramic solid that will meet or exceed all current Waste Isolation Pilot Plant (WIPP) Waste Acceptance Criteria (WAC) and EPA land disposal restriction (LDR) criteria. The determination of the desired composition and performance characteristics of the final waste form product is necessary to establish the materials thermal processing conditions and technology to be used. Various glass/ceramic waste form materials have been considered, compared with the waste stream composition, and a recommendation made for the use of a form of iron-enriched basalt (IEB).

In examining possible glass/ceramic host solids for the stabilization and immobilization of buried TRU mixed wastes, this study has considered the phosphate, borosilicate (BSG), and high alumina-silicate glasses, as well as the iron-enriched basalt, Synroc, and other glass-ceramics. The glassy forms are amorphous (or vitrified), have physical features like window glass or pyrex, and may be translucent or opaque. The ceramics are mostly crystalline (devitrified or rock-like) and have physical features like river rock, lava rock, or granite. Glass-ceramics can be transformed into predominantly glassy or predominantly ceramic forms by the method of processing. Different forms will have different leach characteristics and other properties depending on the composition of the crystalline and surrounding vitrified (glass) phases in the waste form.

From a final waste form product performance standpoint, parameters affecting product performance, such as chemical stability, waste form leachability, thermal stability, mechanical durability, impact resistance to the generation of breathable fines, radiation damage resistance, and environmental compatibility have been identified to be characterized and optimized. Processing parameters such as slag/melt temperature and viscosity, electrical and thermal conductivities of the melt, waste solubility, melt corrosivity and volatility of high vapor pressure hazardous species must be considered to produce the desired waste form in an effective and efficient manner.

The BSG silica-based glass waste form has been approved for the immobilization of radionuclide-bearing high-level waste (HLW) and, as such, represents a standard of comparison in this study. A qualitative comparison of the performance of various glasses and glass-ceramics is given in Table S-2. Phosphate glasses are durable, but have poor thermal stability and low solubility for many waste components and the glass melts are highly corrosive. Borosilicate glasses melt at lower temperatures (900-1200°C) and as a result reduce volatilization of hazardous materials, and are less corrosive to the melter. BSG has good long-range chemical stability, thermal stability, mechanical stability, and, therefore, good environmental compatibility. The silica based glass-ceramics, ferro-alumina silicates (iron-enriched basalt or IEB), and the high-alumina silicate waste forms usually have

Figure S-3. Relative mass (left) and volume (right) fractions of the TRUW, entrained soil, underburden soil and overburden soil for Pit 9. Areas are similar because mean specific gravities are approximately two.

Table S-2. A qualitative comparison of the properties of various glasses and glass-ceramics.

<u>Waste Form</u>	<u>Stability</u>						
	<u>Process Temperature</u>	<u>Mechanical</u>	<u>Thermal</u>	<u>Chemical</u>			<u>Metal Tolerance</u>
				<u>HLW</u>	<u>LLW</u>	<u>TRUW</u>	
Phosphate glass	L	P	P	P	*	*	-
Borosilicate glass (BSG)	L	G	G	G/E	G/E	*	P
Pyrex	M	G	G	E	*	*	-
Aluminosilicate glass	M	E	E	G	*	*	F
Glass-ceramics	M	E	E	G/E	G/E	*	G
Iron-enriched basalt (IEB)	H	E	E	*	G	G	E
IEB4	H	E	E	*	E	E	E
Synroc	H	E	E	E	*	*	-

Key: E = Excellent G = Good F = Fair P = Poor - = Not available
L = Low (900-1200°C) M = Medium (1200-1500°C) H = High (1500-1800°C)
* = Radioactive species should have similar chemical stability in the given waste form

higher chemical stability, thermal stability, mechanical stability, and environmental compatibility, than even BSG, in part due to their crystalline (rock-like) structure and higher temperature (energy) of formation. IEB is a high temperature silica-based, glass-ceramic with high concentrations of iron and aluminum oxide similar to naturally occurring basalt rock. Its composition variations were originally formulated based on various combinations of average TRUW and soil at the RWMC at the INEL. IEB4 is an IEB variation with small additions (1-10%) of Group IV elemental oxides (Zr and Ti) postulated to further increase the leach resistance of TRU and LL nuclides. Synroc is a titania based ceramic with a large concentration of Zr and Ti oxides and is made in a high pressure, lower temperature hot isostatic pressing process. High process pressures, low process throughput capability, and the additional host material stream (titania) required are present show stoppers for the Synroc process in this application, even if it may provide the best performance of any glass/ceramic waste form considered. The metal tolerance in Table S-2 indicates the ability of the waste form to oxidize and dissolve a significant amount of the most prevalent metals, e.g., iron and aluminum. Again the higher temperature glass-ceramics have the ability to dissolve more iron and aluminum oxides in the matrix.

The BSG waste form, approved for immobilization of radionuclide-bearing, high-level wastes, has the advantage of lower processing temperatures; but the lower temperatures are incapable of melting iron (at $\geq 1538^{\circ}\text{C}$) and metal oxidation rates would be very slow. BSG becomes extremely corrosive in this high temperature range. Further, the average TRUW material stream does not have a composition similar to BSG. Waste loadings would have to be small, perhaps $< 10\%$, to produce a BSG waste form. The result would be an increase in total waste volume of 5 to 10 times the original waste stream.

The buried TRUW has an average composition similar to the iron-alumina silicates, which when melted with or without added INEL soil yields the waste form material developed and known as iron-enriched basalt (IEB). IEB, as a final waste form, can accommodate higher waste loadings than BSG and has an associated increased process robustness for accommodating the expected range of heterogeneous input waste stream materials.

The IEB final waste form possesses the following desirable characteristics as compared to BSG: (a) both fine grained and coarse grained IEB final waste forms have demonstrated a much better leach resistance than BSG, (b) IEB waste forms generally exhibit better mechanical and thermal stability than BSG, (c) the IEB fabrication process has high tolerance (acceptance) for all metals, including high melting temperature metals, (d) the IEB waste form and processing is very accommodating to the expected highly heterogeneous buried waste material and varying compositions, (e) IEB processes would produce higher volume reduction for the RWMC TRUW streams, and (f) properties of IEB final waste forms are comparable to the natural geological basaltic rock analogue.

Some limited existing IEB studies indicate that the addition of small amounts of ZrO_2 enables crystals of $\text{UO}_2\text{-ZrO}_2$ to form in the IEB solid solution to form an even more leach-resistant material. This IEB variation material is herein given the name IEB4. Without ZrO_2 present, uranium and plutonium precipitate as separate oxides in the residual glass phase allowing them to be more easily leached than if contained in the ZrO_2 crystalline solid solution phase. It is expected that the TRUs will behave with ZrO_2 in a manner similar to uranium; but this behavior remains to be demonstrated in tests.

System Processing Scenarios

Processing system scenarios integrating various components and melters have been developed. The factors influencing processes within the melter are also discussed and R&D requirements delineated. The processing scenarios pivot around the SDS Incinerator and Melting system. All the scenarios presented are believed capable of destroying hazardous organics and producing an appropriate final waste form to stabilize TRU elements and other hazardous noncombustible.

Sorting Options A, B, C, D, and E represent A) no separations and no incinerator, B) separation of combustibles, C) separation of noncombustibles, combustibles, and metals, D) separation of bulk metals only, and E) no separations with an incinerator for the entire input waste stream. Soil disposition varies depending on the scenario. The sorting can be relatively limited (10-20%) because of the robustness of the processing components. Special case (highly-radioactive and large objects) are assumed to have been sorted out for special processing prior to entering the thermal processing input waste stream.

Scenario I essentially represents the SDS scenario on Incineration and Melting with Postsort of the TRUW & LLW. It utilizes the SDS Retrieval, Soils Processing, and Metals Decon Subsystems. Combustibles, noncombustibles, metals and soil are sorted for processing (Option C). The final waste forms are packaged, assayed, and temporarily stored pending final disposal in a TRUW, Reclassified LLW, or LLW repository.

Scenarios II, III and IV are variations on Scenario I employing the various SDS subsystems in different configurations. Scenario V assumes BSG as an objective and uses borosilicate glass frit and develops a BSG waste form instead of the natural IEB waste form where possible.

The presently recommended scenario from this study is II-E, as shown in Figure S-4. It is very similar to the example processing system discussed earlier and illustrated in Figure S-1. Scenario II-E is a no-sort option which includes both an incinerator and a melter. Scenario II-D is a close second choice and differs from Scenario II-E only in that bulk metals are sorted out for separate metals decon-treatment prior to incineration of the remaining waste streams. The metals separation is an added stage that may not be too complicated and may prove to be beneficial when more detailed design analyses are done. Third on the list is Scenario II-A with no sort and no incinerator, which uses the melter to do both the pyrolysis/oxidation of combustibles and the melt/vitrification of all noncombustibles. Advantages are the no sorting and fewer components, countered by a potentially much more complex process monitoring and control system.

Scenario II, Option E, is the highest priority because it requires a minimum of sorting (no sort other than Special Case), the simplest control of incinerator and melter, only one melter, and maximum safety and maintenance. It requires a less complicated retrieval system (to be determined by others) than the SDS Retrieval Subsystem, one that sorts out overburden soil which may be clean and passes the waste stream and entrained soil to the sizing unit (<50 mm or 2 in.) with an intermediate assay for safety. The contaminated underburden soil is routed to either the soils processing system (to be determined by others) or the melter, if needed. After sizing, the waste stream is routed to a thermal desorber with the pyrolyzed gases going to the incinerator for additional pyrolysis and partial combustion. The solids go to a high-temperature, oxidizing-slag, arc/plasma-heated melter. The metals may be surface oxidized, melted, and tapped from the bottom of the

Scenario II – Simple Retrieval – Over Under Burden Soil Separation

- 1) Credible assays need to be performed.
- 2) Combustibles will be one of the largest problems for production.
- 3) Ion-Enriched Basalt (IEB) is the final waste form.

Project No. 01555

Figure S-4. Scenario II-E, the most highly recommended incineration and melting system scenario.

melter or totally oxidized and dissolved into the slag as found to be necessary in testing. Any combustibles leaving the incinerator will be routed to the incinerator and offgas treatment system, as appropriate.

If separate TRUW disposal is selected, the output slag normally cast as a monolith could be fritted to a size potentially more amenable to an assay (to allow separating TRUW, Reclassified LLW, and LLW, if needed). It has been shown that a water quench may become contaminated under these conditions, requiring secondary treatment. The TRUW frit would be remelted or fused, heat-treated to obtain the optimum final waste form, and poured into appropriate packaging. It is preferable to pour the slag into a monolith in the final packaging and use controlled cooling to obtain the optimum final waste form, if an acceptable assay can be performed.

The melter processes need to be tested to confirm current expectations and to determine how to minimize HVPM carryover, including TRU and LL radionuclides. Oxidation of the metals followed by slow diffusion of the HVPM through a thick slag or foaming layer is expected to reduce the loss into the offgas significantly. Any volatilized toxic or radioactive materials will be collected in the offgas treatment, assayed, dissolved in BSG in a low-temperature Joule-heated melter, and packaged for disposal. Collection may be by condensation/solidification or other specific process (e.g., for Hg). These are to be determined for specific materials later.

It should be noted that Scenario II-A employs a pyrolyzing-gas, high-temperature, oxidizing-slag, plasma/arc-heated melter that replaces the incinerator and the nonpyrolyzing melter of Scenarios II-D and E. This scenario has been partially demonstrated in early test series at the INEL/MSE-Butte Component Development Integration Facility (CDIF), where RWMC soil and simulated metal, combustible, and TRU waste have been processed in an oxidizing high-temperature, plasma-heated melter. The combustible organics were oxidized in the primary chamber with negligible or no sooting. Although an afterburner is required to ensure meeting destruction removal efficiencies required by EPA for hazardous organics and PICS. The metals at a 3/1 metals-to-soil mass ratio were completely oxidized. The slag cast into drums went through a 1-2 day cooling period with a resulting microstructure that was predominantly crystalline (ceramic/rock-like) material, with very little vitrified (glassy) material. Prior experiments with INEL soil and some diesel fuel resulted in a predominantly glassy material. The waste form compositions from this plasma-heated melter (PHM) are essentially duplicates of what was found a decade ago in the INEL IEB research, using a high-temperature Joule-heated melter (JHM).

Melter Processes

There are several primary within-melter process issues that influence the product of the process and the capability of the melter. As presently identified, these are 1) melt fluidity viscosity, 2) electrical conductivity, 3) materials corrosion/erosion, 4) slag chemistry and TRU retention, 5) slag chemistry and HVPM metals retention, and 6) controlled cooling for devitrification.

Fluidity

The composition and temperature of the melt determine its viscosity, and thermal and electrical conductivity—hence, the fluidity and uniformity of the melt. Increasing the silica or alumina content increases the viscosity and decreases the fluidity. Adding fluxes, such as alkali (Na, K, etc.) or alkali earth (Ca, Mg, etc.) compounds decrease the viscosity. Alkalis are dissolved into the glassy phases and not the crystalline, from which they have a susceptibility to readily leach and affect the

leachability of other dissolved substances. As a result, alkali content in the slag should be minimal. The addition of zirconia or zircon to the IEB melt to form a solid solution with U-238 and TRU will raise the temperature required to maintain fluidity. Figure S-5 illustrates the effect of adding flux to the slag melt.

Electrical Conductivity

Joule-heated melters require the electrical conductivity of the melt to be in an acceptable narrow range in order to obtain the optimum heating. If it is too low, the current will be too low, and the I^2R heating too low. If too high, the bath will be short circuited and will not heat as broad a volume. Melted metal collected at the bottom of the bath can short out the electrodes. Because of this constraint on electrical conductivity (and viscosity), Joule-heated melters are limited to a relatively narrow range of composition changes around the design point. This limitation is not amenable to the wide variations in RWMC waste streams expected. An extensive sorting, sampling, and control system would have to be developed to enable Joule-heated melters to be utilized for processing the SDA/RWMC TRUW streams.

In arc/plasma-heated melters, the viscosity is controlled by temperature and the electrical conductivity is not a major factor. Transferred arc and plasma torch-heated melters do have a Joule-heating component; but arc/plasma radiation, strong arc-generated convection, and conduction heating at the electrode attachment region are usually the dominant heating mechanisms. The main disadvantage of the arc/plasma-heated melters for waste processing is the potential for increased vaporization of HVPM at the higher processing temperatures utilized.

Corrosion

Corrosion can occur at the refractory wall near the slag surface, usually due to convective currents in the slag and oxidation or other chemical reactions among the gas, slag, and refractory materials. These problems are accelerated at higher temperatures. With the intense energy disposition possible with plasma/arc heating, the melter walls can be water cooled and a skull of the slag material built up to protect/replace the refractory. These problems are melter configuration and materials dependent.

Corrosion of the electrodes can be a problem in both JHM and PHM. Water-cooled copper electrodes in high-powered plasma torches typically operate for 300 h. Consumable graphite electrodes in arc-heated melters can be oxidized unless operated in a reducing mode or coated to reduce surface oxidation. Oxidizing-slag, pyrolyzing-gas phase melters experience less corrosion than totally oxidizing reactors. A small JHM with nitrogen cooled walls operated for over 2200 h in producing IEB at the INEL on molybdenum electrodes. Each melter configuration has its advantages and disadvantages which must be understood for proper design and testing in new applications.

Table S-3 presents a matrix of waste forms versus melter types. The waste form composition dictates an approximate operating temperature range, which along with the type of electrodes used, determines allowable redox states to minimize corrosion. The type of refractory or use of a water-cooled skull is also based on the composition and temperature range. Table S-3 also indicates the types of waste streams treatable for the temperature ranges given.

N92 0027

Figure S-5. Illustration of the effect of adding flux to the slag melt.

Table S-3. Processing options for using various Joule-heated and plasma-heated melters to make different viable waste forms.

Final Waste Form	Temperature Range	Melter Aspect	Joule-heated Melter	Arc/Plasma-Heated Melter		Waste Streams Treatable
				Transferred-Arc	Nontransferred	
BSG	Low 900-1200°C	Electrodes Atmosphere Melt Refractory	Inconel OX/RED OX/RED Most	Graphite --/RED OX/RED Most	Metal OX/RED OX/RED Most	Combustion Ash Noncombustibles Most soils
ASG G-C	Medium 1200-1500°C	Electrodes Atmosphere Melt Refractory	Moly OX/RED --/RED Alumina	Graphite --/RED OX/RED Alumina	Metal OX/RED OX/RED Alumina	All Above Plus Basaltic Soil Metallic Aluminum
IEB IEB4 Synroc	High 1500-1800°C	Electrodes Atmosphere Melt Refractory	Not Available	Graphite --/RED OX/RED WC Skull	Metal OX/RED OX/RED WC Skull	All Above Plus Zircon Sand Titanate Sand Metallic Iron

Key:

ASG - Aluminosilicate glass IEB - Iron-enriched basalt OX - Oxidizing conditions
 BSG - Borosilicate glass IEB4 - IEB + Group IV elements RED - Reducing conditions
 G-C - Glass-Ceramics SYNROC - Zr,Ti (not Si) based ceramic WC - Water cooled

Slag Chemistry and Retention of TRU Nuclides

The slag melt must be able to dissolve the TRUs and incorporate them in its matrix. The TRU metals are extremely reactive and form insoluble oxide compounds in the glass matrix or oxide solid solutions with alumina, titania, and zirconia in crystalline phases. Tailoring the slag chemistry so that ceramic phases are achieved to retain the TRU species in solid solution is highly desirable.

Slag Chemistry and Control of HVPM

The slag chemistry process (materials, compositions, temperature, pressure, time, mixing) is the most important part of the melter operation because it deals directly with the fabrication of the final waste form material and its performance characteristics. There are several important parameters to be considered in the fabrication of an acceptable high-integrity final waste form, one is the retention of the HVPM. The slag must be able to retain an acceptable fraction of the high vapor pressure metals within its matrix. The volatilization of the HVPM during processing is closely related to the redox state and the temperature of the melt. It is desirable that the volatilization of the HVPM be minimized even at high temperatures. Tailoring the slag chemistry to produce high temperature ceramic phases which will retain these species, such as Pb, Zn, Cd, etc., in stable compounds or solid solutions is highly desirable. Detailed tailored-design studies of the slag chemistry are needed to enable optimization of the retention of HVPM in the slag. The offgas system must be designed to trap any transported HVPMs.

Vitrification/Devitrification Processes

Controlled cooling would allow a manipulation of the vitrification and devitrification processes in the slag to produce the desirable durable ceramic phases with an engineered grain size. These controlled cooling processes have been shown in INEL IEB research to produce a final waste form with much superior product performance characteristics. Typical cooling procedure is to cool the slag to the recrystallization or nucleation temperature (perhaps 950°C) for a period of one to two hours, then raise the temperature about 100°C for 4-8 hours to increase the crystal growth rate, followed by a rapid quench to retain the nonequilibrium state microstructure at ambient temperature. The procedure and recrystallization temperature are dependent on composition and Redox state in the slag. Appropriate testing needs to be done to determine optimum procedures for typical waste slag compositions.

Some Initial Melter Test Series Results

In selecting a conceptual melter design, the most fundamental question is: Can it melt the expected mix (range) of INEL buried waste and contaminated soil? Several recent limited test series have yielded information relevant to this fundamental melter question for INEL wastes.

No recent test results from JHM applications for typical INEL wastes/soils are available. An initial series attempt was begun; however, JHM manufacturers indicated that quite a bit of flux would be needed to melt the soil and they could not handle much metal. High temperature JHM would require development. This was consistent with past work at the INEL with a lab-scale, high temperature JHM that indicated temperatures of 1300-1500°C can be reached to melt INEL soil/waste in a JHM, but with severe consequences to electrodes and refractory (reliability issues). JHM for lower temperature ranges are available, are relatively simple to design and use, and give good low temperature (1050°C) glass waste forms.

INEL soil with metals has been vitrified in tests in a pot melter at the Plasma Energy Corporation (PEC) with a nontransferred plasma arc/torch. Also, slag from the ACT (soil plus diesel fuel) and RWMC (soil, metal, diesel fuel, and wood chips) test series at INEL/MSE CDIF at Butte, MT, was generated in the Retech plasma centrifugal reactor with a transferred plasma arc torch. The PEC test slags were rapidly cooled (1-2 h) and found to be mostly glass phase with some small crystal. Leach tests for toxic metals were well within toxicity characterization leaching procedure (TCL₂) requirements. The ACT test series was cooled slowly (1-2 d), and had a much larger fraction in crystalline or ceramic phase. The RWMC slag samples were also cooled slowly (1-2 d) and were almost all crystalline phase. All the metal and the organics had been oxidized. The RWMC series tests used wide variations in input feed composition, demonstrating the robustness of the basic process. The minerals and structure of the PHM-generated slag were very similar to the high temperature JHM slag generated on the INEL IEB research a decade ago. The results of these tests are very encouraging in that PHM clearly can be used to make a good waste form from the typical RWMC waste and rock mixture and that the knowledge gained from prior research on IEB formed using a JHM is applicable to PHM-generated IEB. Either type of melter can be used as appropriate to generate the required waste form. It appears relatively easy to get excellent waste forms from high temperature plasma-heated melters, but the extent of HVPM loss from the melt needs to be further investigated in any higher temperature melter. Additional melter evaluation tests are clearly needed.

Conclusions and Recommendations

The average TRUW waste stream at RWMC has the composition of an iron-enriched basalt, without adding soil. Adding soil still gives a waste form that is an IEB. Attempting to use or generate waste form compositions other than IEB, such as BSG, would result in low waste loadings and not take advantage of the natural features of the TRUW in RWMC. There are no existing commercial melter systems on the shelf that can be used today to demonstrate application to RWMC wastes and generate IEB. There are, however, high temperature plasma- and arc-heated melters well demonstrated for metal ores processing that are expected to be demonstratable for INEL buried waste applications. There are lower temperature JHMs demonstrated for use on glass and HLW. These would require high temperature development work. If the melting of structural metals is required, a high temperature PHM will be required. Melting of INEL mixed wastes and soils, even without metals, will require a medium to high temperature range, 1350-1500°C, more easily achieved with a plasma/arc-heated melter than a JHM. Ash from the incinerator and residue from the offgas treatment system could probably be treated in a low temperature JHM, possibly using BSG frit. The final waste form can be put into an optimum IEB glass-ceramic form via a controlled cooling process. An integrated system design concept presently recommended is shown as Scenario II-E, with no sorting, a thermal desorption/incineration step for combustibles with an afterburner to ensure complete combustion, melting of the noncombustible portions of the waste soils input with surface oxidation of metals, and free reduced metals tapping. Any high vapor pressure metals carried over in the offgas will be condensed and filtered for separate treatment, perhaps in a low temperature melter step.

The following R&D topics need to be addressed in the near future for completion of development and pilot-scale demonstration tests on a reasonable schedule: (a) crucible tests of the transport and disposition of HVPM (including Cs-137) and metal oxides in high-temperature (1500-1800°C) processing, (b) crucible and melter tests of the retention and dissolution of TRUW and reconfirmation of uranium in zirconia-augmented over the range of incoming waste compositions and slags, including the effect of the redox state in the slag and its influence on the HVPM, as well as

controlled cooling processes and their influence on the phase composition of the final waste form, (c) crucible and melter tests to study metal oxidation and dissolution in the melter in both surface and total oxidation modes, (d) crucible and melter tests to confirm refractory/skull corrosion and protection effects, and (e) melter tests to confirm and resolve expected electrode corrosion/erosion effects. Further design studies, safety related studies, and establishment of a verified set of melter design evaluation tools (models) are needed.

Thermal Processing System Concepts and Considerations for RWMC Buried Waste

1. INTRODUCTION

1.1 Background

This report presents the determination of a preliminary conceptual process systems design, and related processing conditions considerations, for thermal technologies based treatment of Idaho National Engineering Laboratory (INEL) Radioactive Waste Management Complex (RWMC) buried wastes. Early conceptual definition of remediation processes is necessary to allow for the focused and iterative evaluation and development/demonstration of the treatment processes and the enabling process technologies (process equipment).

From the early 1950s through 1972, low-level waste (LLW) generated at the INEL and low-level alpha emitting wastes (defined as transuranic wastes or TRU) were buried in pits and trenches at the Subsurface Disposal Area (SDA) of the RWMC. In 1972 this practice was stopped and the Department of Energy (DOE) began segregation of the wastes, placing TRU wastes in retrievable surface storage at the Transuranic Storage Area (TSA) of the RWMC. Most of the transuranic wastes were generated in the production processes for nuclear weapons at the Rocky Flats plant. Because of the nature of these processes, the TRU wastes contain listed and characteristic hazardous materials as well as radionuclides and are, therefore, categorized as mixed (radiological and hazardous) wastes.

In 1989 the INEL was placed on the Environmental Protection Agency's (EPA's) National Priority List, which requires remediation of the SDA using the Comprehensive Environmental Response Compensation, and Liability Act (CERCLA) decision process. Using the CERCLA process, a remedial action option can either be "no action," in situ treatment and disposal, or ex situ treatment and disposal. A "Preliminary Systems Design Study" (SDS)¹ was conducted in 1990/91 to provide a top-level conceptual remediation systems basis for identifying and focusing waste technology development/demonstration efforts in line with INEL Environmental Restoration buried waste remediation problem needs. The SDS considered four treatment categories related to the final waste form performance: treatment in place, processing to a waste form acceptable for disposal at the DOE's Waste Isolation Pilot Plant (WIPP), processing to a waste form that satisfies EPA's criteria for land disposal restrictions (LDR), and processing to a leach-resistant, high-integrity, vitreous/crystalline (glass/ceramic) waste form (that satisfies all requirements). Of 73 treatment system alternatives identified and screened, 12 concepts were selected and then evaluated based on the stage of technology development, the need for future research and waste-specific demonstration, programmatic and technical risks, schedule requirements, and costs. Life-cycle cost comparisons indicated that the in situ treatments cost the least (no retrieval cost), but these are not within the scope of the present study. Among the ex situ treatments, the costs were similar for all processes. The ex situ Incineration and Melting with (low-level waste) LLW Postsort process system option was identified as producing a waste form which will meet all the WIPP, LDR, and leach/integrity conditions and received the highest overall system concepts ranking [tied with in situ vitrification (ISV) and Retrieval]; hence, this system was chosen as a starting point for the present more detailed work on incineration and melting treatment processes and technologies.

The thermal processing systems and technologies considered herein are focused on, but not limited to, the incineration and melting system process technologies and options recommended by the SDS. Processes associated with Joule-heated melters (JHM) and arc/plasma-heated melters (PHM) have been considered. Processes affecting the melting or dissolution of the mixed waste streams (pretreatment), the microstructure and durability characteristics of the final waste form (posttreatment), and offgas treatment, in addition to the internal melter processes, have been considered.

1.2 Overview

Design and development of a waste treatment process requires the identification and consideration of incoming materials (waste streams) characteristics, output product requirements/criteria (final waste form and performance), and the iterative match of capability of enabling process technology/equipment to the desired process conditions. The purpose of the work reported herein is to provide the next level of thermal processing systems investigation and conceptual design beyond the SDS.

In particular this study was intended to provide a basis for evaluation of the key technology components, particularly the melter, within a thermal processing system context, and to lead to defining preliminary functional and operational requirements for the conceptual design of system components. This study has, therefore, included several separate but related parts.

The study has examined the available buried waste description data in an attempt to better define the incoming waste streams for thermal process conceptual design. This is reported in Section 2 and includes definition of material types, amounts, potential processing problems, whether sorting is needed/desirable, and how these factors influence melter design and processing. Two preliminary design bases waste stream classifications are proposed, representing the range of extremes (an "As Found" mixed waste stream classification and an "As Separated" waste stream classification) to consider for processing.

The study has examined the final product of the thermal process, that is the final waste form product options and performance criteria within the context of the requirements for producing a highly-leach resistant durable glass/ceramic that will meet the DOE requirements for WIPP, the Department of Transportation (DOT) nuclear waste transportation requirements, the EPA LDR requirements, and have capability for meeting future more stringent requirements. Section 3 reports these final waste form considerations. Variation in composition and volume of the final waste form based on different waste streams is considered. These compositions are compared to known glass, glass-ceramic, and ceramic compositions to determine the melting process operating conditions and probable slag and final waste form properties. Appropriate materials characterization tests for the waste form are suggested to verify that the characteristics meet stated objectives for physical and chemical performance.

Considering the waste streams and desired final waste form, Section 4 identifies and compares several potential thermal processing system scenarios/configurations utilizing available melter technologies beginning with and pivoting about the baseline SDS case. Factors influencing processes within the melter are also discussed and key development/demonstration requirements identified. Processing considerations include both the preliminary system design of components and processes within the melter. Incineration will use conventional techniques and components. Various scenarios for the system design using conventional components are presented, as well as a recommended

scenario. The types of melters which should work under the particular processing conditions are delineated. Smelters and melters of similar materials are in common practice but none have completed process applications demonstrations/development for the particular waste streams being considered here. Critical processes within the melter are discussed and aspects of processes requiring research and development (R&D) to ensure successful processing are identified. The effect of nonhomogeneous feed composition is considered. The processing results are integrated with results from the reports focusing on other aspects of the TPT project, including: a survey of prior research at INEL on the iron-enriched basalt waste form,² the assessment of present melter JHM and AHM/PHM capabilities,³ and the survey of modeling melter gas and slag phases for understanding and control purposes.^{a,b} Finally, melter and crucible tests are proposed and prioritized in order to resolve key questions related to optimizing operation of the melting system processes.

In Section 5 several recent test series results related to the melter thermal processing systems issues are briefly discussed.

Section 6 then provides a final summary of conclusions and recommendations.

a. S. Paik, "Melter Models for the Thermal Processing of Mixed Wastes," WTD-92-33, January 1992.

b. R. L. Williamson, "Slag/Melt Modeling Capabilities at INEL," Letter report, January 1992.

2. CLASSIFICATION OF INPUT WASTE STREAMS

The classification of input buried waste streams is important to determine the material categories, how the materials need to be processed, where the potential processing problems exist, and the quantities of materials expected. Two general classifications will be considered. The first will be the average no-sort or "As-Found" in the ground case, as obtained from recent reports on the contents of the SDA. The second will be an "As-Separated" case, which separates combustibles, noncombustibles, metals, and soil, as in both the presort and postsort of LLW from TRUW as recommended in the SDS Report (see Reference 1). The two cases are considered, then comparisons made, and considerations for appropriate waste streams to be input to the incineration and melter processing scenarios are recommended.

2.1 As-Found Classification

2.1.1 Basis for the As-Found Classification

The classification of input waste streams is based on information from existing summaries of waste description data for the SDA at RWMC. The main references used were Vigil⁴ and Arrenholz and Knight,^{c,d} which also referred to prior studies. Of major interest are Trenches 1-10 and Pits 1-6, 9, and 10 because they contain TRUW. Many of the other trenches and pits contain only LLW, and are not the focus of this project. The history and contents of these trenches are described in more detail in the above references. Figure 2-1 presents an overview of the major activities at RWMC related to this work. Trenches 1-10 were filled with INEL MFP/LLW, RFP TRUW, and various off-site wastes from July 1952 until November 1957. The wastes were not segregated by type. At this time the Rocky Flats Plant (RFP) waste was increasing and it was decided to use pits. In the pits, the INEL/LLW and the RFP/TRUW were segregated, but were often located in the same pit. Prior to 1963, the waste had been stacked in the trenches and pits. Between 1963 and 1969 the waste was dumped in the pits in order to save cost and limit worker exposure. Since 1970, the RFP TRUW has been stored in the TSA. The contents in drums from Pits 11 and 12 were relocated to the TSA circa 1978. The TRUW in the SDA was rated at greater than 10 nCi/g; whereas, in the TSA the rating was greater than 100 nCi/g.

The specific data used as background for this report is included in Appendix A for reference. Additional detailed information on the contents and the location within the trenches and pits that will be useful during actual remediation is being generated by Waste Technology Development Department (WTDD) personnel.

c. D. A. Arrenholz and J. L. Knight, "A Brief Analysis and Description of Transuranic Waste Disposal in the Subsurface Area of the Radioactive Waste Management Complex at the INEL," WTD-90-016, November 1990.

d. D. A. Arrenholz and J. L. Knight, "Historical Report of Transuranic Waste Pits and Trenches at the Subsurface Disposal Area of the Radioactive Waste Management Complex at the INEL," WTD-91-027, August 1991.

N92 0079

Figure 2-1. A schematic overview of the major storage activities at RWMC related to this work.

2.1.2 Initial As-Found Classification

The classification of waste streams generated in this report is based predominantly on Tables A-9 and A-11. The classification is for the purpose of defining the type and approximate amount to be processed in order to determine the necessary processes. It is not the purpose of this work to determine quantitative flow process conditions. Table 2-1 provides a classification of the materials in the selected trenches and pits as determined here from the prior tables. The data for the trenches is incomplete at this time. It can be seen that in the various pits there is a wide variety of classes of materials, but the pits are relatively consistent in "composition" (neglecting amounts), with a few exceptions in certain pits. As an example, all the pits have TRUW (Pu and Am), LLW (U, Co-60, Cs-137, Sr-90, etc.), inorganic sludge (hydrated metal oxides), steel and other metals with low reactivity, construction materials, cemented organics, and miscellaneous containerized organics.

Contents of some of the pits may not be sufficiently well known to be identified in the sources used, so only items that are known to be absent should be dismissed. An example is the lack of nitrate inorganic sludges in Pits 1-3 and 5 because they were not received from RFP until 1967, by which time Pits 1-3 and 5 had been closed. Pits containing metals (Na, NaK, Pb, Zn, Hg, Li, etc.) with special processing requirements appear to be Pits 2, 3, and 9, but Pits 4, 5, 6, and 10 also contain similar metals, but in as yet undetermined extent. Much of the Li and Hg is in batteries and may very well be sorted out. NaK is a liquid-metal coolant, but is a solid at room temperature.

Other special or unique processing may need to be applied to handle chloride, fluoride, and radium salts (Pit 2), hydrochloric and hydrofluoric acids (Pits 2 and 9), sodium hydroxide (Pit 9), animal carcasses (Pits 2 and 3), Butyl stearate (Pit 3), and some phenyls (Pits 1, 6, and 10). Most of the other material types are in a sufficient number of pits (and probably trenches) that they should be handled by the mainline process.

2.1.3 Proposed As-Found Classification

A review of Table 2-1 indicates that most of the trenches and pits have similar types of materials as a result of the nature of the sources: RFP/TRUW and INEL/LLW. For similar reasons, the composition of the waste materials depending on the ratio of TRUW to LLW is similar with notable exceptions, i.e., the INEL SL-1 waste, the RFP Recovery Facility fire, etc.

The proposed As-Found classification for input waste streams is based on Pit 9 because more explicit information about contained materials is presently available (from the above references) than for any of the other pits or trenches. Pit 9 does not apparently contain the halogen salts of Pit 2, the animal remains of Pits 2 and 3, butyl stearate of Pit 3, or the phenyls of Pits 2, 6, and 10. The various materials have been put into 18 categories in Table 2-2. The table also lists volumes and masses based on data from Table A-11 for Pit 9. Volumes and masses were converted using density data from Table A-10 and other sources.⁵ Though speculative because volume concentrations are not known precisely, approximate densities are necessary to get an estimate for the processing. Figure 2-2 illustrates the relative mass fractions of Pit 9 in a pie chart. There is considerable uncertainty surrounding the values shown in Table 2-2, and this must be recognized when considering melter processing.

Table 2-1. Preliminary tabulation of materials found in buried waste in selected trenches and pits (see footnote d).

	Trenches										Pits									
	1	2	3	4	5	6	7	8	9	10	1	2	3	4	5	6	9	10		
Metals														x	x	x		x		
Na, NaK, Mg,														x				x		
Pb, Zn														x	x			x		
Hg, Li														x				x		
Other														x	x			x		
TRU (α -emitters)																				
Pu, Am														x	x	x	x	x	x	x
LLW (β/γ -emitters)																				
U-235 238														x	x	x	x	x		
MAP, Co-60, etc.														x	x			x		
MFP, Cs-137, etc.														x	x	x		x	x	
Tritium, Th, Cf,...														x	x	x				
Inorganic Sludges																				
741-2 Hydrous oxides														x	x	x	x	x	x	x
(+ Li, Hg batteries?)																				
745 Na/K Nitrates																x		x	x	x
74R Cemented Nitrates																				
Inorganics																				
Machinery, SL-1/Fire waste														x	x	x	x		x	x
Construction, Fire Matls														x	x	x		x	x	
746 Empty oil drums in cartons																x		x	x	x
NaOH																			x	
Acids (HCl, HF)														x				x		
Asbestos																			x	
Salts																				
Chlorides, fluorides														x						
Radium salts														x						
Organics-Cemented																				
743 Degreasers, coolants														x	x	x	x	x		
Regal, CCl ₄ , Oils, PCBs,																				
Solvents																				
743 Alcohols, Acids, Versenes														x		x	x	x		
Organics-Miscellaneous																				
Oils, Freons, Ethy. Glycol, ^a																x	x	x	x	x
Animal carcasses														x	x					
Butyl Stearate, Meth. 400																x				
Misc. solvents														x		x	x	x	x	x
Tetraphenyls, diphenyls,...														x			x	x		

a. Some of these may be cemented (in with the 743 waste).

Table 2-2. Proposed As-Found classification of input waste streams. Mass/Volume data is from Pit 9 with estimated conversions from Table A-10.

<u>Material Category (Pit 9)</u>	<u>Specified Mass or Volume</u>	<u>Calculated Estimate</u>	
		<u>Mass (kg)</u>	<u>Volume (m³)</u>
1. Na, NaK, Mg (Na Comp.)	3,469 kg	3,469	1.9
2. Pb, Zn (Pb in Pit 9)	7,033 kg	7,033	0.62
3. Hg, Li (Li)	238 gal	478	0.91
4. TRU	16.85 kg	16.85	0.00085
5. LLW	11,700 kg	11,700	0.59
6. Hydrated oxide sludge	16,075 gal	65,662	61
7. Na/K nitrate sludge	30,149 gal	252,678	114
8. Machinery, construction metals, steel drums	658,622 kg	658,622	428
9. Construction bricks, concrete, asbestos	87,467 kg	87,467	83
10. NaOH	859 gal	6,948	3.3
11. Acids (HCl, HF)	1,255 gal	4,728	4.8
12. Cemented organics (cement only)	4,182 gal	16,694	15.8
13. Miscellaneous organics, combustibles (incl. #12)	18,724 gal	20,172	71
14. Organics in silicate sludge	85,535 gal	1,086,781	362
15. Halogen Salts	0 gal		
16. Animal remains	0 gal		
17. Butyl stearate	0 gal		
18. Phenyls	0 gal		
Total		2,222,449	1,146

Figure 2-2. Relative mass fractions of material categories of Pit 9.

2.1.4 Potential As-Found Process Considerations

If the relative masses and volumes of the other pits are similar to Pit 9, as assumed above, the large majority of the mass of the waste in the pit is composed of (a) organics in a calcium silicate sludge, followed by (b) low-reactivity metals, (c) the nitrate sludges, and (d) the hydrated oxides. This sum comprises over 80% of the mass and excludes contaminated or clean adjacent soil. The TRUW and LLW components comprise less than 0.5% of the waste mass. It must also be recognized, however, that various materials may be concentrated locally; hence, large swings in waste streams of retrieved concentrations could occur.

A preliminary discussion of general incineration and melting processing methods and/or problems resulted in the following. Note that organics are to be combusted, "solid" metal oxides to be dissolved in the slag, volatile metals and oxides to be collected in the offgas system, and other inorganic salts to be converted to oxides or collected in the offgas system. The TRU, LL, Na, NaK, Pb, Zn, and Li should be readily oxidized, if not already oxidized or separated but by some other process. The Hg, Cs, and ZnO will likely appear in the off-gas and must be collected, along with any other volatile oxides or metals. The hydrated metal oxides and calcium silicate sludge should not present significant problems. The nitrate sludges will have to be treated carefully to prevent explosive reactions in the reactor. The material safety data sheets (MSDS) indicate that the nitrates could explode when heated. Preprocessing at lower temperatures is an option. The cemented organics can result in irregular combustion reactions and can also erupt or explode; therefore, they should be reduced to two inch or smaller chunks. The process will probably generate a dust which could result in explosions if not handled properly. Any uncemented organics may need to be fed into the reactor in appropriate amounts, but should not provide any unusual problems. The same is true of concentrations of acids (HCl, HF) or bases (NaOH). If mixed and heat treated with soil and lime, the HF may be reduced to calcium fluoride, which can be dissolved into the iron-enriched basalt (IEB) more easily than the chlorides. The large amount of steel from machinery and construction could be separated from the slag and tapped. The bricks, asbestos, and other non-metallic construction materials would be part of the slag. The particular chemical form of the materials is not as important as which elements are involved when using incineration and melting processes.

The major potential problem materials are those which cause discontinuities in the process: eruptions, explosions, unwanted (premature) oxidation, or strong reactions in processing units. The major potential contributors to discontinuities are the nitrate sludge (can erupt at moderate temperatures) and the cemented organics (can erupt when heated or oxidized). These materials will probably require separation for special preprocessing. The effects of other materials which may usually be considered to be bad actors (acids, NaK, etc.) are dampened out here because of the large amount of soil which will be processed with these materials. Other potentially toxic materials (e.g., Hg or Cs-137) can be processed in the off-gas which is discussed under processing in a different section.

A preliminary summary of the expected problems and probable solutions is listed in Table 2-3.

2.1.5 Volume Reduction Considerations

The relative mass and volume fractions of TRUW and associated soil are illustrated in Figure S-3. The mass and volume fractions are similar because of similar densities. The various volumes of waste and soil for Pit 9 are summarized in Table 2-4. Estimated volume reductions in the form of a compaction ratio are calculated. It appears that the volume reduction considering only the

Table 2-3. Expected potential problems and possible fixes for the various material categories of the input waste streams. Note that all substances may have radiation-hazard problems. Most of the reactive metals and radionuclides should be in the oxide state.

Material Category (Pit 9)	Expected Problem	Potential Fix
1. Na, NaK, Mg, Li	high reactivity	dilution in soil and oxidize/dissolve in slag.
2. Pb, Zn	high volatility	oxidize/collect in slag or collect in offgas system.
3. Hg/Li batteries	high reactivity	dilution in soil, Hg pollutant collect in off-gas system.
4. TRU (Pu, Am)	α -radiation	detect to limit exposure, oxidize/dissolve into slag.
5. LLW (U, MFP, MAF) Cs-137, etc.	β/γ -radiation	detect to limit exposure, oxidize/dissolve into slag, collect in off-gas.
6. Hydrated oxide sludge	hydrate eruption	dilute with soil and dissolve in slag.
7. Na/K nitrate sludge	high-T reactivity	low-T roast to get oxides, dissolve oxides in slag, NO_x processed in off-gas.
8. Machinery, construction metals, steel drums	none	oxidize and dissolve in slag or tap melt and package.
9. Construction bricks, concrete, asbestos	none	melt and dissolve in slag.
10. NaOH	high reactivity	dilute in soil, oxidize and dissolve in slag.
11. Acids (HCl, HF)	high reactivity	dilute in soil, oxidize and dissolve in slag.
12. Cemented organics	high-T eruption	crush, incinerate, and dissolve ash/oxides in slag.
13. Miscellaneous organics, combustibles	irregular combustion,	preprocess w/wo soil, toxic incinerate (rotary kiln), dissolve ash/oxides in slag.
14. Organics in silicate sludge	proper oxidation	melter off-gas incineration, or rotary kiln, react with oxides and dissolve in slag.
15. Halogen salts	high reactivity	dilution with soil, oxidize, dissolve in slag.
16. Animal remains	contamination	dilution with soil, oxidize, dissolve oxides in slag.
17. Butyl stearate	toxicity	dilution with soil, oxidize, dissolve oxides in slag.
18. Phenyls	toxicity	dilution with soil, oxidize.

Table 2-4. Various volumes and calculated volume reduction or compaction ratios for Pit 9 based on estimated volumes and masses.

<u>Volume Identity</u>	<u>Volume</u>	
	<u>(ft³)</u>	<u>(m³)</u>
Dense Waste (Table A-10)	40,482	1,146
Extraction Volume	342,416	9,696
Container Volume	150,690	4,267
Net Soil with Waste	191,726	5,429
Underburden soil	149,807	4,242
Overburden soil	256,812	7,272
Total soil	598,345	16,943

<u>Compaction Ratio Taken</u>	<u>Value</u>
Soil Only	$\frac{\text{slag(S.G. = 3.2)}}{\text{soil(S.G. = 2.0)}}$ 1.60/1
Waste Only	$\frac{\text{Container Volume}}{\text{Dense Waste}}$ 3.72/1
Waste + Entrained	$\frac{\text{Extraction Volume}}{\text{Waste + Entrained}/1.60}$ 2.13/1
Waste + Entrained + Under	$\frac{\text{Extraction + Underburden}}{\text{Waste + (Entrained + Underburden)}/1.60}$ 1.94/1
Waste + All Soil	$\frac{\text{Extraction + Underburden + Overburden}}{\text{Waste + (All Soil)}/1.60}$ 1.81/1

containers and the contained waste is about 4-to-1. If the surrounding soil (excluding overburden and underburden) is included with the waste, the compaction ratio is about 2-to-1. (The compaction of the soil from its natural field density is about 1.6-to-1.) Including the over- and underburden soil decreases the volume reduction to approximately 2-to-1. The density difference between slag (specific gravity about 3.2) and the soil in the pit (specific gravity about 2.0) giving a volume reduction factor of $3.2/2.0 = 1.6$ has been considered in the above calculations. The minimum volume reduction is, therefore, about 2-to-1, on an average, assumed homogeneous basis. The volume loss of organics and other volatile matter has been neglected in this conservative calculation.

If all the TRUW (without soil) were mixed to obtain a homogeneous waste stream input; combusted to remove the organics, NO_x from the nitrates, and halides; and the remainder oxidized; the final waste form would solidify to a glassy rock with an average composition of approximately 38% silicon oxide, 7.4% aluminum oxide, 34.5% iron oxide, 8.3% calcium oxide, 4.6% magnesium oxide, 4.8% sodium oxide, and 2.4% potassium oxide.⁶ This composition was called the "Average TRU-contaminated Waste" composition for the RWMC and is designated A-0. The "0" indicates the wt% of RWMC (basaltic) soil in the final waste form: A-40 indicates 40% RWMC soil and 60% average TRUW. If the RWMC soil were melted and solidified, it would form a ferro-aluminosilicate glass/rock (partly amorphous glass and partly crystalline rock). The A-0 composition gives an iron-enriched aluminosilicate glass/rock; hence, the composition of the waste is very similar to the soil with designations between A-0 and A-100 spanning the limits.

A-0 will make a good waste form, but a particular melter batch will probably not have the average waste composition. If it does, a 4/1 volume reduction is attainable. If not, the amount of contaminated soil added to obtain an appropriate composition will reduce the volume reduction ratio to no worse than 2/1.

2.2 As-Separated Classification

2.2.1 Basis for the As-Separated Classification

The classification of input waste streams for the As-Separated classification is based on the recommendations of the SDS (see Reference 1). Only two of the treatment systems proposed in the SDS fall within the work scope of the JHM/PHM applications, the incineration and melting with LLW Presort (2-EG-1) and with LLW Postsort (2-EG-4). The difference between the two is that in the first, after retrieval, an on-line assay is made to separate TRUW and LLW wastes prior to other sorting procedures common to both systems. (Figure A-1 gives the process flow diagram for the presort system.) The common sorting procedures occur at different stages and essentially separate into three classes: (a) TRUW for packaging and storage in a TRUW repository, (b) LLW wastes for separate treatment (from TRUW) and subsequent LDR storage, and (c) clean off-gas, water or soils for unrestricted disposal.

The recommendation of the SDS is for the Postsort option (see Figure A-2) because of estimated cost savings. In the Postsort option, the On-Line Assay between TRUW and LLW and, hence, the LLW Processing Subsystem (S-IT-3, as shown in Figures A-7 and A-8) are eliminated. With this option, the disposal options are the same, but the assay and separation of TRUW and LLW occur after the decontamination of metals, incineration of combustibles, and melting and dissolution.

Prior to retrieval, the trench or pit would be characterized by available methods to identify probable locations of concentrations of TRU and LL sources. The Retrieval Subsystem (S-BE-4 as

shown in Figures A-3 and A-4) would then separate the soils from the non-soil containers, machinery, etc. A Soils Processing Subsystem (S-EB-2 as shown in Figures A-5 and A-6) then separates the soil into TRU-contaminated soil, LL-contaminated soil, clean soil, and clean water. The non-soil containers are opened and sorted into metallic, non-metallic/combustible, and combustible streams. The combustibles are shredded and incinerated, followed by ash separation and off-gas treatment. A Metal Decontamination Subsystem (S-EG-1 as shown in Figures A-9 and A-10) sorts into TRUW metals, LLW metals, liquid/residue, and clean water. All TRU-contaminated soil, TRUW metals, combustible ash, off-gas and metal-decontamination liquid/residue, and shredded non-combustible waste are routed to the melting furnace. Final TRUW products are packaged and sent to TRUW storage. LLW wastes are routed to a LLW treatment facility with final disposal under LDR. Clean, treated off-gases, water, and soil are disposed of without restrictions. Additional details are discussed elsewhere (see Reference 1).

2.2.2 Initial As-Separated Classification

The Presort process flow diagram (see Figure A-1) can be expressed in terms of a simplified component waste streams as shown in Figure 2-3. For Postsort, the LLW materials stream would be combined with the appropriate TRUW combustibles, non-combustibles, and metal wastes. Rearranging the materials categories classified in Table 2-2 into the component waste streams results in the preliminary As-Separated classification presented in Table 2-5. The nitrates are included with the combustibles because they are oxidizers, can react favorably with the silicate sludge to form a good final waste form, and can give potential processing problems. The table also lists "soil" on the rough assumption that the TRU-contaminated soil is possibly contained in the net soil in the waste (see Table 2-4), the LLW materials are possibly contained in the underburden soil or equivalent amount, and the clean soil may be equivalent to the amount of the overburden soil. The molecular weights used to estimate the number of moles are given in parenthesis and are based on some component(s) in the material. The soil is assumed to be a "calcium-oxide" basalt. The number of moles is useful in estimating the quantity of additional materials that will be required to complete the reactions or dissolution.

2.2.3 Potential As-Separated Process Considerations

The As-Separated Case represents a first cut at dividing the total waste and related soil to reduce the TRUW storage, to use incineration techniques where possible, and to separate the LLW from clean materials. Considering the comments in Section 2.1.4, it appears that it may be desirable to have more than one incinerator or reactor to convert the TRUW combustibles to desired forms. Also some additional feedstock processing will be necessary with different feedstocks requiring different processes. In brief, the preliminary As-Separated classification appears to be better than the As-Found, but needs additional refinements.

Potential refinements are shown in the preliminary flow diagram of Figure 2-4 which includes features of both the Presort and Postsort options. The combustibles are shown as four streams in Figure 2-4: miscellaneous organics, cemented organics, organics in silicate sludge, and the Na/K nitrates. The animal remains, Butyl stearate, and phenyls of Table 2-5 or other organics not explicitly identified here could be added to one or more of these streams as appropriate. The miscellaneous and cemented organics need to be processed in a crusher or shredder prior to incineration. Ash is recycled to the silicate melter #1 through one of the other pretreatment processors. Off-gas treatment is via traditional mixed waste incineration methods. The organics in silicate sludge are proposed to be mixed with some TRU-contaminated (or other) soil prior to entering the melter to minimize the effect of small eruptions. Additional soil may be added as needed. The nitrates are

15

Table 2-5. Initial As-Separated classification of input waste streams. Mass/Mole data is for Pit 9 as estimated from Tables A-10 and A-11. Pit 9 has no record of LLW from the INEL. The basis for the molecular weight is given in parenthesis.

<u>Material Category</u>	<u>Estimated Molecular Weight</u>	<u>Calculated Estimate</u>	
		<u>Mass (kg)</u>	<u>kg-Moles</u>
<u>TRUW Combustibles</u>			
7. Na/K nitrate sludge	91	252,678	2,777
12. Cemented organics (Portland cement only)	66	16,694	253
13. Miscellaneous organics (incl. #12, assm'd CCl ₄)	152	20,172	133
14. Organics in Ca silicate sludge (75CaSiO ₃ +25C ₂ H ₆ O ₂)	89	1,086,781	12,211
16. Animal remains		0	0
17. Butyl stearate		0	0
18. Phenyls		0	0
<u>TRUW Non-Combustibles</u>			
6. Hydrated oxide sludge (Al ₂ O ₃ ·H ₂ O+Fe ₂ O ₃ ·H ₂ O)	119	65,662	552
9. Const. bricks, concrete asbestos (CaSiO ₃)	116	87,467	754
10. NaOH	40	6,948	174
11. Acids (HCl, HF)	27	4,728	175
15. Halogen Salts	0		
<u>TRUW Metal Waste</u>			
1. Na, NaK, Mg (NaK)	62	3,469	56
2. Pb, Zn (Pb in Pit 9)	207	7,033	34
3. Hg, Li (Li in Pit 9)	7	478	68
8. Machinery, construction metals, steel drums (Fe)	56	658,622	11,761
<u>Radioactive Materials</u>			
4. TRU (Pu-239)	240	16.85	0.07
5. LLW (U-238)	238	11,700	49
<u>Soils (SiO₂·FeO·Al₂O₃·CaO)</u>			
19. Entrained Soil (Assumed TRUW Soil)	290	10,876,093	37,504
20. Underburden Soil (Assumed LLW)	290	8,498,143	29,304
21. Overburden Soil (Assumed Clean)	290	14,568,244	50,235

roasted at low temperature to convert them to the oxides and NO_x . The oxides are added to the melter; whereas, the NO_x needs to be processed to N_2 and O_2 (e.g., by the dielectric barrier discharge^{7,8,9} or the gliding arc discharge¹⁰ or more conventional methods). The material from the melter would be packaged, assayed, and stored (see Figures A-1 or A-2).

The non-combustibles are also shown as four streams in Figure 2-4: hydrated metal oxides, construction materials (bricks, concrete, asbestos), bases (NaOH), and acids (HCl , HF). Other non-combustibles could be added to one of these streams. The halogen salts could probably be added to one of these streams or to a combustible stream if strong reaction effects are expected. For the four streams, the pretreatment in a crusher is similar. Mixing with soil could probably be done sequentially in the same crusher while feeding the oxide melter #2. Additional soil can be added as needed to give the appropriate melt composition.

The TRUW and/or LLW metallic wastes would be processed by the Metals Decontamination Subsystem, with the LLW metals being packaged for LDR disposal, TRUW metals, liquids and residue going to the TRUW metal melter #3, and clean water being recycled for use in various subsystems.

Not considered in the above simplified scheme are details in the processes, including off-gas treatment of high vapor-pressure metals (HVPM), the addition of fluxes to facilitate dissolution or affect viscosity, and packaging considerations. Offgas collection and treatment options are being considered by others.¹¹ The actual methods, which have to be specific to the resulting process, need to be resolved in a later design stage.

Several melters have been considered in this preliminary waste stream analysis. A number of such systems may be needed to handle the quantity of waste in the proposed SDS time period. Each melter system will predominantly handle similar types of waste streams so that the monitoring and control system techniques will be similar on each melter and for each set of operators. Systems could be modified to handle other streams depending on loading factors and maintenance.

2.3 Recommended Classification of Waste Streams

It is premature to determine the optimum waste stream classification prior to additional information on the details of the processes. This must involve a systems design analysis that integrates the input waste streams, the desirable final waste product, and the processes necessary for particular waste streams. From the As-Separated discussion, it appears that a number of different material streams could be input sequentially or concurrently to the same preprocessor (shredder/crusher) and be blended and melted to obtain the desired high quality waste product. The amount of some of the components will depend to some extent on the amount of other components and the particular process or recipe to be used; hence, the input waste stream matrix if extensive sorting is to be used will also have to be determined later.

Preliminary reviews of this report have indicated that it will be very difficult and expensive to do sorting and much more to do sophisticated sorting. Based on the discussion above it appears that a "logical" sort of combustibles and noncombustibles per Table 2-5 may not be practical. If sorting is to be done at all, a more practical sorting could run most of the questionable materials into a thermal desorber/incinerator system first as "combustibles," with the identifiable concrete, bricks asbestos, etc. as "noncombustibles," and easily sorted metals (by magnets or mass/conductivity methods). The soils could be added as needed for buffering or composition control. The resulting

distributions are shown in Table 2-6. The radionuclides are assumed to be distributed throughout the other materials.

The mass of the noncombustible waste stream is now about 10% of the combustible stream and could be included to provide additional buffering and simpler sorting. Adding the structural metal stream to the other two would increase the heating requirements, but this metal would not melt or vaporize, hence, the incineration process (prior to the afterburner) could provide a means of cogeneration to preheat the metal and noncombustibles with the combustion heat just prior to entering the melter. Melter process time can be thus substantially reduced, giving greater throughput per melter. If the combustion air is countercurrent to the waste stream, it could also act as the thermal desorber near the entrance of the incinerator. With this integrated waste stream, sorting is unnecessary. The TRU-contaminated soil can be either injected separately or with the heterogeneous waste stream to obtain an appropriate final waste form.

Table 2-6. Recommended as-separated classification of input waste streams.

<u>Material Category</u>	<u>Estimated Molecular Weight</u>	<u>Calculated Estimate</u>	
		<u>Mass (kg)</u>	<u>kg-Moles</u>
<u>TRUW Combustibles</u>			
1 Na, NaK, Mg (NaK)	62	3,469	56
2 Pb, Zn (Pb in Pit 9)	207	7,033	34
3 Hg, Li (Li in Pit 9)	7	478	68
6 Hydrated oxide sludge ($\text{Al}_2\text{O}_3 \cdot \text{H}_2\text{O} + \text{Fe}_2\text{O}_3 \cdot \text{H}_2\text{O}$)	119	65,662	552
7 Na/K nitrate sludge	91	252,678	2,777
10 NaOH	40	6,948	174
11 Acids (HCl, HF)	27	4,728	175
12 Cemented organics (Portland cement only)	66	16,694	253
13 Miscellaneous organics (incl #12, assm'd CCl_4)	152	20,172	133
14 Organics in Ca silicate sludge ($75\text{CaSiO}_3 + 25\text{C}_2\text{H}_6\text{O}_2$)	89	1,086,781	12,211
15 Halogen Salts		0	0
16 Animal remains		0	0
17 Butyl stearate		0	0
18 Phenyls		0	0
<u>TRUW Non-Combustibles</u>			
9 Const bricks, concrete asbestos (CaSiO_3)	116	87,467	754
<u>TRUW Metal Waste</u>			
8 Macninery, construction metals, steel drums (Fe)	56	658,622	11,761
<u>Radioactive Materials</u>			
4 TRU (Pu-239)	240	16.85	0.07
5 LLW (U-238)	238	11,700	49
<u>Soils ($\text{SiO}_2 \cdot \text{FeO} \cdot \text{Al}_2\text{O}_3 \cdot \text{CaO}$)</u>			
19 Entrained Soil (Assumed TRUW Soil)	290	10,876,093	37,504
20 Underburden Soil (Assumed LLW)	290	8,498,143	29,304
21 Overburden Soil (Assumed Clean)	290	14,568,244	50,235

3. CRITERIA AND REQUIREMENTS FOR FINAL WASTE FORM

3.1 Summary

Development of a host solid for the immobilization of nuclear wastes and non-nuclear hazardous waste has focused on various vitreous/ceramic waste forms including borosilicate, high silica glass (Pyrex), high alumina silicate glasses, iron-riched basalt (IEB), glass-ceramics, and phosphate glasses. Consideration of all parts of the waste disposal system ensures that the final product will safeguard the public, and that the production process used will be safe, efficient, and environmentally sound to operate. The system engineering development approach requires that parameters affecting product performance and processing conditions be considered simultaneously. Parameters affecting product performance, such as chemical stability, waste form leachability, thermal stability, mechanical durability, impact resistance to generate breathable fines, radiation damage resistance, and environmental compatibility, must be ensured and optimized, relative to processing parameters such as melt temperature and viscosity, electrical and thermal conductivities of the melt, waste solubility, melt corrosivity, and volatility of high vapor hazardous species.

Numerous system research approaches have indicated that borosilicate glasses (BSG) are, overall, the most studied glasses for immobilization of nuclear wastes. Some phosphate glasses are highly durable; but the glass melts are highly corrosive to the melter even at 900°C, have poor thermal stability, and have low solubility for many waste components. On the other hand, iron enriched basaltic (silica composition ranges from 40-60 wt%) waste forms, glass-ceramics, and high alumina silicates have high chemical stability, high thermal stability, high mechanical stability, and good environmental compatibility, but their associated high melting temperatures potentially increase the volatilization of hazardous waste species during processing. The fabrication of these final waste forms requires the use of very high temperature melters. The borosilicate glasses melt at much lower temperatures than other high temperature waste forms and are generally less corrosive to the melter. The low melting temperatures of borosilicate glasses minimize excessive volatilization of hazardous species from the melt.

However, there are serious drawbacks to the fabrication of BSG final waste forms. The BSG fabrication process requires a known waste stream composition and is incapable of handling a highly varying heterogeneous waste streams. Because of the low processing temperatures, BSG processes cannot handle refractory materials such as iron and basaltic soil. The fabrication of BSG final waste forms required large additions of B_2O_3 , alkaline oxides, alkaline earth oxide, and glass frits. The INEL RWMC buried TRU mixed wastes and the associated contaminated soil are heterogeneous and their compositions vary between extremes. Retrieving and converting the RWMC buried TRU mixed wastes to BSG is impractical and impossible. The process would require costly efforts to separate all the high melting metals, a large addition of glass forming materials, and a tight control of the waste stream compositions. The large quantity of glass forming materials needed to fabricate BSG will not produce a volume reduction of the RWMC buried wastes and, potentially, the process would produce a high volume of the final waste form.

Based on the System Design Study (see Reference 1), the waste form must be a leach-resistant, high quality synthetic glass or rock and must satisfy the general requirements established for high-level waste forms to be disposed of in deep geological repository. The final waste form will also comply with the TRAMPAC (transportation and packaging) requirements. From the design stand point, the final waste form must possess the following characteristics: (a) chemical stability, (b) thermal stability, (c) mechanical durability, (d) high leach resistance, (e) high impact resistance to generate breathable

lines, (f) macroscopic homogeneity in terms of overall waste form properties performance, (g) high waste loading capability, and (h) high stability to internal α , β , and γ radiation damage.

From the design stand point the final waste form must meet the following specific requirement assumptions: (a) plutonium and other TRUs will be dissolved, oxidized, and chemically incorporated into the silicate melt, (b) low-level wastes and/or fission products will be dissolved, oxidized, and chemically or physically incorporated into the melt, (c) HVPM will be either incorporated into the silicate melt or volatilized from the melter and collected down-stream of the melter unit for separate disposal, (d) the final waste form should enable a high concentration of Fe and Al to be chemically dissolved because they are the major components of the INEL TRU waste stream and this would yield maximum volume reduction, and (e) the final waste form will not contain organic residues and water of hydration so that hydrogen generation due to radiolysis will not become a problem because the final waste form is produced from very high temperatures.

In view of the above general and specific requirements, iron-enriched basalt (IEB)¹² is a suitable final waste form to immobilize the INEL RWMC buried TRU mixed wastes. The IEB final waste form possesses the following desirable critical characteristics (see Reference 6) as compared to BSG: (a) both fine-grained and coarse grained IEB final waste forms have demonstrated a much better leach resistance for uranium than BSG and high silicate glasses, (b) IEB waste forms generally exhibit better mechanical and thermal stability than BSG, (c) the IEB fabrication process has high tolerance for all metals, including high melting temperature metals, (d) the IEB waste form is very accommodating to highly heterogeneous waste streams with varying compositions, (e) IEB processes produce very high volume reduction for the RWMC TRU waste streams, and (f) properties of IEB final waste forms are comparable to the natural basaltic rock analogue.

The INEL soil is basaltic and is among the waste streams at the site; therefore, the basaltic soil should be considered as the host matrix to fabricate IEB for immobilization and stabilization of the RWMC radioactive mixed hazardous wastes. The IEB previously studied at INEL should be reinvestigated and pursued more vigorously as a viable final waste form for the INEL buried radioactive wastes.

3.2 Nuclear Final Waste Form Development

Development of final glass waste forms for the solidification of nuclear waste began at different times in the U.S., Canada, Europe, and the USSR. Different glass formulation and processing methods were developed. The system approach to final nuclear waste form development must consider the parameters affecting the product performance. Table 3-1 indicates desirable characteristics of the final waste form product. Table 3-2 lists desirable conditions during the processing of the waste in a melter.

The borosilicate glass formulations were developed in the U.S. between 1956 and 1957. The aluminosilicate glass formulations were simultaneously being developed in Canada in 1957. Phosphate-base glasses were the last to be investigated and the first to be abandoned as a final waste form for nuclear waste. The evaluation of phosphate glasses demonstrated that the positive aspects of processing, e.g., low melting temperatures, were out weighed by other negative processing aspects—melt corrosiveness to the melter system and poor product performance. Later, glass-ceramic such as IEB (see References 6 and 12) and ceramic such as Synroc¹³ (a titanate-based material) were developed as final waste forms for the immobilization of nuclear wastes. These waste forms have compositions that parallel the natural analogs which are stable in geological time scale. These

Table 3-1. Desirable final waste form characteristics.

Desirable product characteristics
Chemical stability
Thermal stability
Mechanical durability
Impact resistance to generate breathable fines
Macroscopic homogeneity in terms of overall properties performance
Waste form insolubility
Resistance to radiation damage
High TRU and fission products retention in the final waste form
High hazardous metal retention in the final waste form
Ease of waste form formulation

Table 3-2. Desirable process conditions for waste form development.

Desirable process characteristics
Appropriate Melt temperatures
Minimum Melt corrosivity
Maximum Waste loading
Appropriate Melt thermal conductivity
Appropriate Melt electrical conductivity
Appropriate Melt viscosity
High reproducibility
Ease of radiation shielding and equipment handling
Minimum volatilization of hazardous high vapour pressure metals

types of ceramic and glass-ceramic final waste forms are much more leach resistant under parallel test conditions and provide higher levels of assurance over a wider range of geological disposal temperatures than those applicable to borosilicate waste glasses. At present, research and development into all types of final waste forms are still on going. Figure 3-1 attempts to present an overview of the historical development of nuclear final waste forms.

3.2.1 Borosilicate Glass (BSG)

The first glasses formulated for use in nuclear waste disposal were investigated by Goldman and others as early as 1956.^{14,15,16} They examined the calcium-aluminosilicate with boron oxide added to achieve a pourable glass at 1300°C. The quality of the glass did not suffer from the incorporation of ZrO_2 and Fe_2O_3 , which were present in the nuclear wastes. Eliassen and Goldman (see Reference 15) considered the most promising vitreous systems for future development were borosilicate-based glasses, e.g., $CaO-Al_2O_3-B_2O_3-SiO_2$ and $CaO-Na_2O-Al_2O_3-B_2O_3-SiO_2$, because these glasses were pourable at 1300°C and their quality did not suffer from the incorporation of nuclear waste materials.

Although the original BSG formulations were developed in the U.S., further development and testing of the vitrification process during the early 1960s were carried out primarily in Britain and Europe.^{17,18,19} In the mid-1960s, the Waste Solidification Engineering Prototypes (WSEP) program was initiated at Pacific Northwest Laboratory (PNL) and demonstrated the overall ease of possibility and compositional flexibility of BSG for high-level wastes (HLW).²⁰ Simultaneously, PNL demonstrated the capability of Joule-heated glass-melters (see Reference 20). Other waste producers such as Savannah River Laboratory (SRL) built upon both European and U.S. experiences and utilized BSG as the preferred final nuclear solid waste disposal form.²¹ Borosilicate glasses are alkali aluminosilicate which are fluxed with boron. The lower alumina content and the presence of boron lowers the melt viscosity and, hence, the processing temperature to below 1150°C. This is low relative to that of other aluminosilicate glasses. In general practice, the viscosity of the melt is kept near 100 Poise for easy pouring. Besides lowering of the melt viscosity at a given temperature, boron also increases the solubility of many waste constituents in the silica-based glass.²² While maintaining thermal and mechanical stability²³ of the glass, boron only decreases the chemical stability slightly²⁴ relative to the highly durable, but much harder to process, high alumina silicate glasses.

The typical BSG²⁵ (see Table 3-3) currently in use for the solidification of nuclear waste is very different from the original Pyrex BSG. Since the borosilicate waste glasses contain 15-30 wt% waste, much of the chemistry is still dominated by the chemistry of the alkali oxide-silica-boron oxide system. The alkali oxide is mainly Na, K, or a combination of Na and K. Quite often, the alkali oxides are tailored to include alkaline earths, such as Ca and Mg, to produce a glass melt with slightly higher melting temperatures. Alkaline earths are not strong charge carriers and will not increase substantially the electrical conductivity of the melt—a requirement for Joule-heated melting, while maintaining the melt fluidity. From Table 3-3, the compositional differences between the borosilicate waste glasses and Pyrex show that Pyrex has a much higher silica content and, hence, melts at a higher temperature. Pyrex is an extremely durable glass due to its high silica content.²⁶ The high alumina silicate glasses, IEB, and glass-ceramics have comparable silica composition but the melting temperatures of these hosts are considerably higher than BSG because of a higher composition in alumina and the alkaline earth oxides. In particular, the alkaline content in IEB is one of the lowest among other silicate glasses and its melting temperature is substantially higher than most other glasses.

Figure 3-1. Historical development of the nuclear final waste forms.

Table 3-3. Typical range of waste glass composition.

Oxide wt%	Pyrex	BSG	AlSG	G-Cer	PG	PbFePG	IEB	Synroc
SiO ₂	81	25-50	33-40	32-60	0-6	0-0.25	35-57	
B ₂ O ₃	13	9-22		1-11				
P ₂ O ₅		0-2			30-55	25-42		
Na, K, Li	4	8-19	18-22	0-13	5-25	1-2	0-7	
Mg, Ca		0-6	13-16	2-33			0-18	14-16
BaO								0-7
Fe ₂ O ₃		1-20			0-2	6-13	10-35	0-25
Al ₂ O ₃	2	0-10	26-30	10-24	0-35	1-2	8-17	0-7
TiO ₂		0-3	0-3	0-2.1				59-65
ZnO		0-22		0-13				
PbO		0-50			0-30	36-53		
ZrO ₂				0-21.4			0-14	11-14
FPS		0-30	0-5	0-20	0-30	0-0.25	0-35	0-8
TRUs	10	>1	0-7	0-10	1-2.5		>20	
RE - as TRU surrogates								0-28
<div> <div>BSG - Borosilicate Glasses</div> <div>AlSG - High Alumina Silicate Glasses</div> <div>G-Cer - Glass Ceramics</div> </div> <div> <div>PG - Phosphate Glasses</div> <div>PbFePG - Lead Iron Phosphate Glasses</div> <div>IEB - Iron Enriched Basalt</div> </div> <div> <div>FPS - Fission Products</div> <div>TRUs - Transuranics</div> <div>RE - Rare Earths as TRU surrogates.</div> </div>								

Table 3-4. Characteristics of different waste forms compared to BSG.

TYPES OF WASTE FORMS							
<u>Product Stability</u>							
	<u>Pyrex</u>	<u>BSG</u>	<u>PG</u>	<u>AlSG</u>	<u>G-Cer</u>	<u>IEB</u>	<u>Synroc</u>
Chemical	excellent	good	good	excellent	excellent	excellent	excellent
Thermal	good	good	poor	excellent	excellent	excellent	excellent
Mechanical	good	good	poor	excellent	excellent	excellent	excellent
<u>Process Characteristics</u>							
	<u>Pyrex</u>	<u>BSG</u>	<u>PG</u>	<u>AlSG</u>	<u>G-Cer</u>	<u>IEB</u>	
Melt temperature	>1400°C	<1150°C	<1050°C	>1350°C	>1450°C	>1500°C	
Melt corrosivity	high	average	high	high	high	moderate	
Melt viscosity	moderate	average	low	moderate	moderate	high	
Waste solubility	moderate	high	moderate	low	high	high	
Limit volatility	moderate	good	good	moderate	poor	poor	
<div> <div>BSG - Borosilicate Glasses</div> <div>AlSG - High alumina silicate Glasses</div> <div>G-Cer - Glass Ceramics</div> </div> <div> <div>PG - Phosphate Glasses</div> <div>IEB - Iron-Enriched Basalt</div> </div>							

Table 3-3 indicates the upper and lower oxide composition limits in the final waste form. Table 3-4 compares the system characteristics of different waste glasses. The borosilicate melts are generally less corrosive to the refractory materials of the glass melter than other nuclear waste glasses due to lower temperatures of fabrication or the absence of P_2O_5 . The technology used for commercial waste glass fabrication can, therefore, easily be applied to the process of borosilicate glass. Under these considerations, borosilicate glasses exhibit favorable product performance as well as ease of processibility.

The product stability and the process characteristics of different final waste forms use BSG as a reference baseline for comparison. The total amount of alkaline or phosphoric oxides (see Table 3-3) in each waste form and its corresponding melt temperature were used as baseline criteria to rank the melt corrosivity to the melter system and the melt viscosity. The process characteristics for Synroc was not compared with other waste forms because the material was fabricated and consolidated under hot pressed conditions well below its melting temperature.

3.2.2 High Alumina-Silicate Glasses

The major advantages of high alumina silicate waste glasses are the excellent chemical, thermal, and mechanical durability due to the high silica and alumina content. The disadvantages are the high melting temperatures of $>1350^\circ\text{C}$, which require a higher temperature processing environment and may lead to higher volatilization of hazardous species and, therefore, limited retention of these wastes in the glass (see Reference 22). Melt corrosivity of the high alumina silicate glass is comparable to that of the commercial Pyrex glass and is greater than the borosilicate glasses due to a higher fabrication temperature. An evaluation of process conditions for the high alumina silicate glasses indicates that while they have superior product characteristics than BSG, they are more difficult to process.

3.2.3 Iron-Enriched Basalt (IEB)

Another class of the aluminosilicate glass-ceramic which is considered for nuclear waste immobilization is the iron aluminosilicate, an analogue to natural basaltic rock. Of particular interest are silicate melts relatively low in alkali metals, i.e., $<10\%$ R_2O where R is Na or K. The foremost objective is to immobilize heavy metals within a stable iron aluminosilicate matrix. A slag composition with particular promise for fixing heavy metals is $SiO_2-Al_2O_3-FeO_x-MO$, e.g., an iron-enriched basalt investigated at Corning Glass Works²⁷ and the INEL.²⁸ M is either an alkaline metal, an alkaline earth, or a combination of the two groups. Properly formulated and processed, this slag resists chemical and physical decomposition. In geological terms, basalt is an igneous crystalline rock, a slag formed in nature from mixtures of oxides. Basaltic magma, cooled slowly, formed crystalline phases rather than amorphous phases. Two major components are plagioclase feldspar and monoclinic pyroxene. The ratios of FeO/Fe_2O_3 (or Fe^{2+}/Fe^{3+} cations) apparently are optimal between 0.1 - 0.5 (see Reference 27) in terms of avoiding undesirable foaming and precipitation of metallic species during processing.

A basalt contains a relatively high amount of SiO_2 , Al_2O_3 , and Fe_2O_3 . These higher valency cations can exchange for other heavy metal ions with comparable ionic sizes and valency. The pyroxene incorporates greater concentrations of the oxides, such as CaO , MgO , FeO , which can exchange for other heavy metal ions with comparable ionic sizes and valency. In terms of melt composition formulation for metal incorporation, Table 3-5 (see Reference 27) shows the ionic size

Table 3-5. Cation size indices and valency for ionic exchange reaction (see Reference 27).

K(I)	0.03	Fe(II)	0.14	Fe(III)	0.22
Na(I)	0.06	Cu(II)	0.14	Mo(IV)	0.28
Ba(II)	0.07	Ni(II)	0.14	Ti(IV)	0.28
Pb(II)	0.08	Mg(II)	0.14	AL(III)	0.35
Ca(II)	0.09	U(IV)	0.19	Si(IV)	0.48
Mn(II)	0.13	Zr(IV)	0.20	As(V)	0.60
Zn(II)	0.14	Cr(III)	0.22	P(V)	0.62

indices and valency for exchange reactions. The Roman numerals in the parenthesis are the oxidation states of the metal ions.

Thus, Zn(II), Cu(II), and Ni(II) tend to substitute for Fe(II) and Mg(II), and Cr(III) to substitute for Fe(III) in a crystal lattice. In feldspar and pyroxene, the alkali metals are acceptors for Ba(II) and Pb(II); also the alkali earth ions and Fe(II) are acceptors for all other ions with similar size and charges. The silicate melt should contain a wide range of higher valency oxides such as Zr(IV), Ti(IV), Al(III), and Si(IV) to accept the various heavy metals in the feedstock. Excessive addition of sodium and calcium oxides to an aluminosilicate is known to result in more rapid weathering of the silicate matrix. Incorporating a reasonable or controlled portion of the Na(I), K(I), Ca(II), Fe(II), and Mg(II) ions with the silicate can actually enhance the environmental compatibility by providing the substitutional or interstitial sites for other hazardous metal ions. There can also be important process benefits; increasing the aluminosilicate alkaline or alkaline earth metals content typically lowers both its viscosity and in some cases the liquids temperature. As a result, slag mixing and uniformity in the melter operation can be improved, which can be important for producing homogeneous and environmentally stable slag.

One INEL study of IEB (see Reference 28) for nuclear waste incorporation found IEB had high capability to incorporate radioactive nuclei and other toxic metals. Figure 3-2 shows the results of the INEL's IEB studies. IEB can dissolve up to 14 wt% of zirconia, which in turn has high solubility for UO_2 . When uranium dissolves and oxidizes in the IEB melt, it forms extensive stable solid solutions with ZrO_2 in the IEB matrix.

3.2.4 Glass-Ceramics

Although glass-ceramics have also been examined as hosts for the solidification of nuclear waste, these forms proved more difficult to process and are not as flexible toward variations in waste composition as BSG.^{29,30,31,32,33,34,35,36} The objective of the development of glass-ceramics was to provide chemical, thermal, and mechanical stability superior to the borosilicate glasses. However, intergranular glassy phases often formed in the ceramic materials, especially when alkali-containing waste was processed. This intergranular glass limited the product stability and durability.^{37,38} The chemical durability of glass-ceramics was found to be comparable to BSG.³⁹ The concept of using a glass-ceramics matrix for the immobilization of the radioactive waste is accomplished by tailoring the dissolution of the waste in an assemblage of mineral phases.⁴⁰ In the glass-ceramic formulation, the idea is to use additives to alter the waste composition, thus tailoring the wastes chemically so that the desired hosts for the radionuclides are produced after solidification. This class of synthetic materials includes the silicate-titanates and silicate-phosphate glass-ceramics.

3.2.5 Phosphate Glasses

The effort and intensity in the research and development of phosphate-based waste glass for radionuclide immobilization was completely dwarfed by the development of borosilicate glasses. The relatively lack of major development in phosphate glasses has been attributed to the lack of industrial usage of these types of glasses and hence the lack of commercial experience and technology such as exists for the various silica-based glasses. The attractive low melting temperature of the phosphate glasses is offset by the corrosivity of the melt to the melter system and the ease with which the glass is devitrified (see Reference 25). Phosphate glasses were also attractive because Mo and SO_4^{2-} were more soluble than in borosilicate glasses (see Reference 36). Compared to borosilicate glasses the phosphate glasses have severe shortcomings. In a demonstration project in 1966, PNL revealed the following shortcomings of the phosphate glass investigated by PNL (see Reference 20) as follows:

Figure 3-2. Tolerance range of major oxides in IEB.

- High volatility of Ru during processing
- Excessive Fe(III) and Na(I) required to adjust the melting point and the melt viscosity
- Extreme corrosivity of the melt — requiring Pt melters and limiting the pouring temperature of the melt into metal canisters
- Low solubility of certain waste components — Al_2O_3 , alkaline earth oxides, and TRUs
- Segregation of fission products in the glass — increased leaching
- Rapid thermal devitrification at temperatures $> 500^\circ\text{C}$ — increasing the risk of leaching by a factor of 1000.

Later, in 1984 lead-iron-phosphate glass was developed as a new, very stable and easily prepared glass for the immobilization of all types of high-level liquid wastes.^{41,42} The corrosion rate of this new glass is at least 100 - 1000 times lower than the corrosion rate of a comparable borosilicate waste glass at $900\text{--}1000^\circ\text{C}$. In addition, the glass could be prepared at temperatures as low as 800°C because of low melt viscosity. Furthermore, the glasses were not adversely affected by large doses of gamma radiation in water at 135°C . It was suggested that the improved chemical and thermal stability was caused by the content and structural role of Fe(III) which strengthened the cross bonding of the phosphate chains in the glass.⁴³ However, melt corrosivity and incompatibility with certain canister materials^{44,45} were observed for this new glass. Even with this new glass formulation, the shortcomings in low waste solubility and rapid devitrification (poor thermal stability) at temperatures above 550°C still persisted. By and large the research and development work on phosphate glasses has been abandoned.

3.2.6 Synroc

Synroc⁴⁶ is a synthetic three-phase crystalline titanate, designed on the basis of known geochemistry, for the immobilization of HLW to higher levels of assurance over a wider range of geological disposal temperatures than those applicable to BSG. The three principal phases, $\text{BaAl}_2\text{Ti}_6\text{O}_{16}$ (barium hollandite), $\text{CaZrTi}_2\text{O}_7$ (zirconolite), and CaTiO_3 (perovskite) can incorporate 10-20 wt% of all components of the HLW into solid solution. The typical weight proportions of these three phases are approximately 40, 35, and 25%, respectively. A minor TiO_2 phase is normally present to buffer the system and maintain the hollandite when significant amounts of Ti(III) are produced during fabrication. Synroc is very leach resistant up to 300°C and it will allow consolidated HLW to be disposed without engineered storage, thus increasing public acceptability for final waste form disposal. The fabrication of Synroc is very different from other final waste form processes because it does not go through a melting process. The process requires the mixing and calcining of HLW (composition well controlled) with fixed amounts of TiO_2 , ZrO_2 , Al_2O_3 , BaO , and CaO . The calcined products are then consolidated by hot-pressing to a high density final waste form at a temperature well below the melting temperature under reducing conditions.

3.2.7 Recommendations

A preliminary survey on nuclear waste glass forms has been completed. Not enough details on each process were given. More in-depth comparison of the advantages and disadvantages of borosilicate glasses, high alumina silicate glasses, glass-ceramics, and iron-enriched basalt should be

done. Both the INEL TRUW and INEL-contaminated soil fall within the range of IEB compositions. Naturally, IEB should be the preferred choice for the final waste form for incorporation of the INEL nuclear wastes. IEB formulations have comparable or better performance characteristics for waste incorporation and retention than the borosilicates glasses. The addition of zirconia to the IEB needs further studies since the formation of zirconia-urania solid solutions will enhance the retention of U and/or TRUs in the waste form. The addition of titania-zirconia to the IEB has the potential of forming major Synroc-like phases in the IEB. These phases will enhance the incorporation and retention of TRUs in the modified IEB waste form. The volatilization of LL and TRU radionuclides from a high temperature melter has not been established. The rare earths (or lanthanides) are good surrogates for uranium and plutonium in establishing the dissolution behavior in the slag and the volatilization from the slag. These areas will need bench studies.

3.3 Criteria for RWMC TRU Final Waste Form

3.3.1 System Design Study Generalized Criteria

There are several Comprehensive Environmental Response, Compensation, and Liability Act (CERCLA) criteria which guided the System Design Study to set the top-level requirements for the final waste form performance characteristics. The CERCLA criteria included the following.

- Overall protection of human health and the environment
- Compliance with appropriate or relevant and applicable requirements
- Long-term effectiveness and permanence
- Reduction of toxicity, mobility, and volume through treatment
- Short-term effectiveness
- Implementability
- Cost
- State acceptance
- Community acceptance.

3.3.2 Desirable Final Waste Form Characteristics and Criteria

Based on the CERCLA criteria, the preliminary SDS identified that the preferred final waste form for TRU waste is a leach-resistant, high-integrity, synthetic glass or rock which can capture TRU waste elements and can meet the general requirements established for a high-level waste to be disposed of in deep geological repository. The final waste form must also comply with the transportation and packaging (TRAMPAC) requirements. The high-integrity final waste form must possess the following desirable properties performance characteristics:

- Chemical stability in high leach resistance
- Thermal stability
- Mechanical durability in high impact resistance to generate breathable fines
- Macroscopic homogeneity for overall final waste form performance
- Least volume
- High stability to internal α , β and γ radiation damage.

From the desirable product properties performance characteristics, a set of specific performance criteria has been generated for the RWMC TRU final waste form. The final waste form performance criteria include the following:

- Plutonium and other TRUs will be dissolved, oxidized, and chemically incorporated into the slag to form a high integrity final waste form which is equivalent to or exceeds the expectation for BSG for the HLW.
- Low level wastes and/or fission products will be dissolved, oxidized, and chemically or physically incorporated into the slag to form a high integrity final waste form which is equivalent to or exceeds the expectation of BSG for the LLW.
- HVPM will be either dissolved/oxidized and chemically/physically incorporated into the slag by appropriate methods, or volatilized from the melter and collected down-stream of the melter unit for separate disposal.
- The final waste form should enable a high concentration of Fe and Al to be chemically dissolved because they are the major components of the INEL TRU waste stream and this would yield maximum volume reduction.
- The final waste form will not contain residue organic materials.
- Potential for gas generation will be nonexistent because there is neither organic residue nor water of hydration in the vitreous/ceramic final waste form which is produced from very high temperatures processing (e.g., $>1500^{\circ}\text{C}$).

3.4 Final Waste Form Evaluation

3.4.1 Materials Characterization Methods

Ex situ thermal processing technology is being considered to treat the soil contaminated with hazardous and radioactive wastes at high temperatures and fix the contaminants in a benign high quality glass or glass-ceramic final waste form. The process involves heating the contaminated soil and wastes with appropriate additives in a high temperature processor to produce a molten slag. Natural convective currents within the melt help to homogenize the stabilized materials. The molten slag cools to a benign and high integrity glass or glass-ceramic final waste form, depending on the cooling rates, chemically and physically resembling natural obsidian or other volcanic rocks. The final waste form can be cast either as monoliths, or as water granulated marbles, or frits. Since the primary purpose of the ex situ thermal treatment process is to stabilize and immobilize nuclear and toxic waste components, the chemical composition and the release characteristics of the final waste forms must be known to determine an accurate performance assessment of the process. Failure to fully characterize the final waste forms from bench, pilot, and field demonstration tests would undermine the credibility of the ex situ thermal treatment process as a method for the INEL environmental restoration program.

Currently, there is a substantial data base on the chemical, physical, and internal radiation damage^{47,48} stability properties of different final waste forms which includes glass, glass-ceramic, and Synroc (see References 13, 46, 48).^{49,50} However, the final waste forms are directly related to the composition of the incoming waste to be treated and the host matrix, the thermal history of materials during reaction, and phases and morphology development during vitrification or devitrification of the melt. Since the INEL soil and waste stream compositions are varied and unique, detailed characterization procedures to qualify the final waste for disposal are required.

The waste forms produced during laboratory, bench, and pilot facility tests will be made using surrogate wastes. Some laboratory, bench, and pilot tests will be conducted using radioactive and mixed wastes. The field demonstration will process the actual mixed radioactive hazardous wastes. When radioactive waste forms are produced, internal radiation effects, along with the other standard tests, will be performed. The data generated will be used to determine how well the ex situ high temperature melting process satisfies CERCLA criteria.

Evaluation of the final waste form performance characteristics will determine the extent to which the CERCLA criteria are met. Characterization of the final waste forms can be divided into three aspects: (a) sampling and bulk characterization, (b) chemical, phase, and morphological analyses, and (c) stability or durability tests. Testing details of the latter two aspects of materials characterization are contained in Appendix B.

3.4.2 Sampling and Bulk Characterization

The primary objective of the product evaluation statistical sampling activities of the bench, pilot, and field demonstration tests are to provide an accurate description of the bulk final waste form and detailed evaluation of the properties of the different phases observed. For the cast monoliths, sampling will be conducted using cores drilled through the monoliths or through a fracture of the monolith. A megascopic physical description of the monolith is the first step in the characterization of that material. The physical description provides the most general information gained during the material characterization processes. A megascopic description of the monolith is important because the sampling strategy of all other characterization techniques cannot be detailed until the type and distribution of the megascopic regions are known. By identifying the major regions of the monoliths by the unaided eye, and stratified random sampling those regions, sufficient data can be generated to determine the chemical, morphological, and durability properties of each region. A megascopic evaluation will also reveal the volume percent of the total that each region represents. This information is required to allow for a bulk mass balance, an indication of potential interfacial reactions, and a determination of the bulk durability.

3.4.3 Chemical, Phase, and Morphological Analyses

The purpose of chemical analysis is to determine the elemental composition of the final waste form as a whole, by regions, and by the phases in each region. The purpose of phase and morphological analyses is to identify the crystallographic phases of the bulk and in the regions. The molten slag is a complex elemental system which can form multiple phases while solidifying. During casting of the monolith, different regions of the cast have different cooling rates and this is reflected by the formation of heterogeneous phases in the monolith. Fast cooling outer regions of the monolithic bulk will vitrify to form glasses while the slow cooling inner regions will solidify into crystalline phases. Due to thermal diffusion effect, some glasses in the intermediate regions will partially devitrify to crystalline materials. The structure and elemental composition of each region will reveal if any waste components have segregated into less durable phases or migrated into interfaces between regions or the grain boundaries of crystalline phases.

3.4.4 Chemical Durability

Chemical durability testing has been discussed by Bates⁵¹ regarding in situ vitrification of INEL buried waste. The discussion can be directly applied to the evaluation of the final waste form from a melter since these final waste forms are very similar. There are currently no specific durability specifications established for ISV/IEB final waste forms. The minimum expected testing requirements

will be those currently established for landfill disposal. Since September 1990, the EPA toxicity characterization leaching procedure (TCLP)⁵² has replaced the Extraction Procedure Toxicity Test (EPTox). Passing the test only classifies the ISV/IEB waste final form as satisfying the RCRA criteria for EPA-designated toxic metals leach characteristics. However, the TCLP test procedures neither address the radioactive components, provide an assessment for the long-term durability, nor make a comparison to other highly durable final waste forms or natural analogs. For each type of the durability tests, all major phases within the ISV/IEB final waste form should be tested, if possible. Where multiple phases cannot be separated, such as when devitrification produces an intimate mixture of different small grain crystalline phases, these multiphase mixtures should be tested as a single phase.

Assessing the long-term durability of the ISV/IEB final waste form is difficult because it requires extrapolation of data from short-term tests to geologic time frames. One method to assess the long-term durability performance is to compare the ISV/IEB waste form to the natural analogs. A number of the natural analogs are similar in composition and morphology to the ISV/IEB final waste forms. These include obsidian, basalt, tektites, and andesites (all of which are millions of years old). The relative durability of many natural and ancient man made glasses have been shown to bracket the durability of waste glasses.^{53,54,55,56} Thus, relating the behavior of the ISV/IEB final waste forms determined from short-term leach tests to the observed behavior of natural analogs provides an excellent means of validating the long-term stability of the ISV/IEB final waste forms. The natural analog also provides a basis for assisting in public acceptance of the ex situ high temperature processes for the INEL environmental remediation program. While the public has little understanding about the durability of the high-level waste glasses, they will have an appreciation for a comparison made of ISV/IEB final waste forms to a "rock" they can pick up in the field that has been exposed to the environment for millions of years.

3.4.5 Physical Durability

The physical durability of the final waste form will be evaluated using a variety of mechanical test methods. The Impact Test reveals the resistance of the monolith during impact to generate breathable fines and is necessary to satisfy TRAMPAC requirements. The Bending Test reveals the fracture toughness of the final waste form. Indentation Tests indicate the hardness of the final waste form. Splitting Tensile Strength Tests give the maximum strength of the final waste form.

3.4.6 Radiation Durability

The radiation damage has long-term effects on the materials properties. The chief sources of radiation in the final waste forms are the β/γ decay of fission products (e.g., Cs-137 and Sr-90) and the α decay of the actinides. β/γ decay of fission products is responsible for the bubble formation (see Reference 49) and the heat generation early in the history of the final waste form. The α decay of the actinides remains important through out the history of the final waste form. The β decay and α decay events can cause three types of radiation damage in the final waste form (see Reference 48): (a) collision cascades which cause atomic displacements and the creation of Frenkel defect pairs due to elastic collisions between nuclear particles (e.g., α - α or α -recoil nuclei), (b) ionization effects associated with high velocity α or β particles, and (c) the transmutation of radioactive parent nuclei into different elements. Of these three effects, the atomic displacement is the most important process which causes atomic-scale rearrangement of the structure and hence leads to the greatest change in chemical and physical durabilities of the final waste forms. Because the mass difference between an α and a β particle is so great, the atomic displacement caused by the β/γ decay is insignificant. The Simulated Radiation Damage Test provides the comparative resistance of the amorphous and the

crystalline phases in the final waste form to atomic displacement and ionization damage due to internal radiation source effects.

3.4.7 Proposed Waste Form Characterization Methods for Tests

Table 3-6 summarizes the available test methods for chemical, irradiation, and mechanical durability evaluation of the final waste forms. It is useful to group the waste form characterization into a short-term and a long-range focus. The focuses are needed to compile data to qualify the final waste forms to satisfy the CERCLA criteria.

The short-term focus is to characterize the properties of the final waste forms produced from the bench studies and the pilot tests based on the process parameters. The results will become a data base for critical evaluation of the ex situ high temperature thermal process and its ability to produce acceptable high integrity final waste forms. The data base will also provide a basis to qualify the final waste form for the CERCLA criteria. The characterization methods recommended for the short-term focus are the following:

- TCLP—required for EPA designated toxic metals
- MCC-3—agitated leach test of powders for all metals, particularly for radionuclides
- ICP
- SEM - EDXS/WDXS - x-ray Maps
- OM
- XRD
- Irradiation tests
- Indentation - hardness test
- Bending - fracture toughness test.

The long-term focus is to characterize the properties of the waste forms from the demonstration tests based on the production parameters determined from the pilot tests. The results will become a data base for critical evaluation to qualify the final waste forms to satisfy the CERCLA and TRAMPAC criteria for permanent dispositions. The long-term focus will include the MCC-1 and impact tests in addition to all the short-term materials characterization methods as follows:

- Impact test—required to qualify the final waste form for TRAMPAC criteria
- MCC—long term static leach test of monoliths for all metals, particularly for radionuclides.

Splitting tensile tests will not be recommended for the evaluation of the strength of the final waste form for either the short-term or the long-term focus because this method is very sensitive to the surface microcrack conditions.

Table 3-6. Summary table of chemical, irradiation, and mechanical durability tests for the final waste forms.

Test Method	Functions
TCLP	EPA regulatory leach test for designated toxic metals
MCC-1	Static leach test for monoliths, reveal leach resistance
MCC-3	Agitated leach test for powders, reveal leach resistance
Forward Rate	Evaluate and predict the dissolution behavior of waste forms
Irradiation	Predict waste form resistance to internal radiation damage
Bending	Determine fracture toughness of the final waste form
Impact	Determine resistance to generate breathable fines, satisfy the TRAMPAC criteria
Indentation	Determine hardness for the final waste form
Tensile	Determine maximum strength of the final waste form

4. WASTE STREAM PROCESSING

4.1 Introduction

Processing considerations are presented for both an overall systems design (see Section 4.2) and a more detailed materials processing (see Section 4.3) viewpoint. The input waste stream considerations are taken from Section 2 and the desirable waste form microstructure and composition from Section 3. The systems design is based on the Preliminary Systems Design Study (SDS) (see Reference 1) as modified by materials processing needs and focuses on requirements for processing major constituents. The detailed materials processing focuses on problem materials and how to control and bind them in a suitable waste form. The Systems Design Study has been extremely valuable by providing a relatively detailed technical assessment of options and estimated costs of the types of process components, subsystems, and overall systems that could be used to generate suitable waste forms.

This chapter takes the analysis for the "incinerator/melter option" one step further by considering more specific input waste stream compositions and process methods required to get a desirable waste form. In the following, the difference between "waste" and "waste soil" needs to be recognized because the buried waste is often separated into waste streams and soil streams (which also contain waste, e.g., TRU-contaminated waste vs TRU-contaminated soil). The topics to be discussed in this chapter are various preliminary systems design component scenarios, appropriate melting processes of interest in the melter or other components, and problem areas in which more information (R&D) is needed to complete the desired design.

4.2 Systems Design Scenarios

4.2.1 General Considerations

Five general systems design scenarios are considered, each of which has several suboptions. The scenarios are modifications of the SDS recommended melting and incineration system with postsort (2-EB-4) for which the process diagram is shown in Figure A-2. The first scenario is essentially identical to the SDS system and represents the base case for comparison. The variations in the systems and options are summarized in Table 4-1. The first four columns are SDS subsystems for retrieval, soils processing, LLW processing, and metals decontamination.

The SDS Retrieval Subsystem (S-BE-4) is composed of two moving buildings 127 by 250 ft long each with space for equipment storage, scooping the earth, conveying, opening the containers, depositing in new containers, container storage, testing, control, power, and maintenance rooms (see Figures A-3 and A-4). The sorting out of highly radiative objects, large mechanical or construction objects, or unusually large containers for special case preprocessing occurs during retrieval. Soil can be separated and routed to the SDS Soils Processing Subsystem (S-EB-2), that thermally desorbs the soil at 450°F, separates the TRU-contaminated soil from the LL-contaminated and clean soil, assays for and separates the LL-contaminated soil from the clean soil, and solidifies (cements) the LLW (see Figures A-5 and A-6). Metals may be routed to a Metals Decontamination Subsystem (S-EG-1) that pretreats, sizes, and decontaminates primarily the surface of the metals as needed (see Figures A-9 and A-10). If presorting of the TRUW and LLW is desired, an on-line assay following the Retrieval Subsystem can be used to separate TRUW and LLW wastes. The latter can be

Table 4-1. Summary of the options included in the system design scenarios.

Scenario	Input Sorting Options												TRUW Soil Options				
	SDS Ret. SS	SDS Soil Proc SS	SDS LLW Proc SS	SDS Metal Decon SS	A	B	NonComb		C	D	E	Options					
							None	Comb				Metal		Metal	None	Melt	Mixed
I. SDS Version (2-EG-4)	Y	Y	N ^a	Y	---	---	---	Y	---	---	---	Y	N				
II. Simple Retrieval Burden Soil Separation	N	N	N	N	Y	Y	Y	Y	Y	Y	Y	Y	Y				
III. SDS Retrieval SS All Soil Separation	Y	N	N	N	Y	Y	Y	Y	Y	Y	Y	Y	Y				
IV. SDS Retrieval SS SDS Soil Processing SS	Y	Y	N	N	Y	Y	Y	Y	Y	Y	Y	Y	Y				
V. SDS Retrieval SS	Y	Y	N	N	Y	Y	Y	Y	Y	Y	Y	Y	N				

a. The LLW Processing subsystem is an available option that was not recommended in the SDS (see Reference 1).

Key:	SDS	System Design Study
	SS	Subsystem
Comb	Combustibles including soil containing organics.	
Noncomb	Noncombustibles including soil not containing organics (thermally desorbed or natural).	
Melt	Soil waste material is melted into a final waste form.	
Mixed	Soil waste material is mixed with other wastes to provide the basic slag material.	

treated by the LLW Subsystem (S-IT-3), that opens packages and sorts the waste stream into metals, lead, sludge, and combustibles/loose materials which are packaged or solidified prior to assaying and disposal (see Figures A-7 and A-8).

A major question with the above is in the ability to assay TRU in objects larger than the size of pebbles or marbles. Such assaying capabilities do not presently exist with confidence. Many of the processes proposed are still under development (R&D) with the resulting capabilities unknown. Other processes add materials to the waste stream which decreases the extent of volume reduction. (The Metals Decon Subsystem has 140 kg units out for every 100 kg in.) Because of this, the best scenarios of the following will include processes which are not dependent on developing new technology, but applying old technology to this new application and attempting to add as little external material as possible.

Table 4-1 also indicates the extent to which sorting options can be used in the various scenarios with sorting (A) and (E) none, (B) only combustibles, (C) noncombustibles, combustibles, and metals, or (D) only metals out from the main waste stream. It is expected that each waste stream will not exclude other stream materials, but will be predominantly the designated waste stream materials. Combustibles include containerized organics, organic-laden soils, cemented organics, and silicated organics, as well as alkali nitrates which are oxidizers. Noncombustibles (e.g., construction materials) include materials known to exclude combustibles and metals.

The reasons for separating into these waste streams will be explained in more detail in Section 4.3, but will be briefly addressed here. The combustibles are to be oxidized into H_2O and CO_2 with any ash, associated calcium silicate, cement, and similar metal oxides going to the melter as part of the slag waste form. The noncombustibles can go directly to the melter as they are metal oxides already and do not have to take up space or energy in the incinerator if sorting is not inconvenient. The metals will have to be oxidized, or at least surface oxidized to remove the surface contamination of TRUW materials, which will require a melter with an oxygen atmosphere, oxygen bubbling through the melt, or equivalent. The high concentration of metals (especially aluminum) will probably result in a higher temperature for the slag fluidity. Control of a combustion chamber with a heterogeneous fuel feed is difficult enough without compounding the problem by trying to control the composition (partitioning) within the melt/slag phase at the same time; hence, the desire to separate into different waste streams.

Other questions, of a political nature, also affect the types of processes required. In the ISV option, the input waste is vitrified in place. The TRUW and LLW are not separated and the cost of environmental remediation are much smaller than when sorting and transportation are required.

The most economical and useful disposition of the soil is also desired. Is it best to melt and package separated TRU-contaminated soil (if the soils processing subsystem is used) or to use the TRU-contaminated soil as the basic waste form to dissolve the other waste materials? The decision is a balance between polluting the nonsoil waste with TRU-contaminated soil, the decrease in volume reduction, the use of LLW soil and probable TRU contamination, and the use/cost of processing additional vitrification material. The TRU-contaminated soil option is included in Table 4-1 as options L (separate melting) and K (mixed together with other waste streams).

The first scenario is patterned after the SDS system 2-EG-4, the Melting Incineration System With LLW Postsort (sort of TRUW from LLW after melting), which will hereafter be referred to as the SDS scenario. The identical system with presorting of the TRUW and LLW waste streams, 2-EG-1, is an alternative, but was not recommended by the SDS report because of the additional cost of the LLW processing subsystem without additional benefits in the resulting waste form. Table 4-1 shows that the SDS scenario includes the Retrieval Subsystem, the Soils Processing Subsystem, and the Metals Decontamination Subsystem, but excludes the LLW Subsystem in lieu of post sorting. The SDS scenario includes Option C (input sorting of combustibles, noncombustibles, and metals) and Option L (the TRU-contaminated soil is melted separately).

In Treatment, the combustibles are incinerated with the appropriate offgas treatment. The noncombustibles go to a melter, in front of which there is a mixer to mix the waste stream with the necessary soil to make the glassy/rocky waste form, ash from the incinerator, residue from the offgas treatment, as well as any fluxes needed to maintain proper melter operation. The metals are routed to the SDS Metals Decon Subsystem from which the TRUW stream and residue goes to the melter and the LLW stream is packaged or solidified. The melter must be an oxidizing melter because of the significant input of metals and, hence, the offgas is oxidized and put into the offgas treatment system. There is no intermediate assay or post-treatment of the final waste form planned in the SDS scenario, but these may be necessary depending on the quality of the assay methods and final waste disposal requirements. The slag waste stream from the melter is packaged, assayed for separation of TRUW from LLW, and separately packaged (TRUW) or solidified (LLW) for disposal. The disposition of reclassified LLW was not included as a separate alternative in the preliminary SDS.

Actual melters run the spectrum from low temperature, pure Joule-heated melters (see Figure 4-2a) through transferred arc-heated melters with Joule, radiative and arc-melt interface heating contributions (see Figure 4-2b) up to nontransferred-arc torches for plasma-convective heating (see Figure 4-2c). Figure 4-3 shows a cut away view of one of the INEL JHM used for IEB research. Figure 4-4 illustrates the difference between (a) transferred arc and (b) nontransferred arc models of operation in a plasma-heated torch. Figure 4-5 illustrates a cross section of the Retech plasma centrifugal reactor (PCR) in operation at INEL/MSE in the plasma-arc furnace experiment

Scenario 1 - SDS Process Incineration and Melting System with LLW Pre or Post Sort [1]

[1] J. L. Mayberry, W. J. Quapp, F. Rezakhanlou, J. C. Del Signore, J. Melter, Preliminary Systems Design Study: Assessment Report, Vol. IV, "Leach Resistance High Integrity Structure Concepts", EGG-WTD-9504-4, June, 1991

Figure 4-1. Scenario 1 - SDS process incineration and melting system with LLW pre or post sort (see Reference 1).

N92 0024

Figure 4-2. Conceptual sketch of electrically-heated melters: (a) Joule-heated melter with the immersed electrodes in the horizontal configuration, (b) an arc-heated melter with 3-phase AC operation and graphite electrodes, and (c) a plasma-heated melter with 1-phase DC operation and both electrodes in the torch.

Figure 4-3. The INEL Joule-heated melter with molybdenum electrodes used for IEB research (see Reference 6).

Plasma torch types

N91 0161

Figure 4-4. Plasma-heated melter torch-electrode configurations: (a) transferred-arc torch with the melt as the cathode and (b) nontransferred-arc torch with both electrodes in the torch.

N91 0172

Figure 4-5. Plasma-heated melter used in the INEL PAFE experiment in the transferred-arc mode with 1-phase DC operation, metal electrode torch, an oxygen lance, and water-cooled skull with a rotating chamber that is slowed to pour the slag (see Reference 57).

(PAFE). The PCR uses a transferred arc torch with an oxygen lance for combustion inside the chamber. The slag is poured out the bottom by slowing the speed of rotation.

Low-temperature melters (900-1200°C) can melt glasses and assimilate waste streams which are not high in metals content, especially aluminum and iron, and are not high in metal oxides or soils with high alumina (alumina-silicates, basalts) or titania/zirconia (e.g., Synroc). These melters are usually termed glass melters. Refractory-lined, Joule-heated melters with Inconel electrodes using a borosilicate glass frit for assimilation of a relatively homogeneous waste stream is one example of a low-temperature (glass) melter. Almost any melter can operate under low temperature melter conditions.

Medium-temperature melters (1200-1500°C) can usually melt various glasses, glass/ceramics and soils. A Ruby-refractory lined, Joule-heated melter with molybdenum electrodes is an example of a low-maintenance, medium-temperature melter. High-temperature melters (1500-1700°C) are capable of melting most ceramics and metals, including iron, basaltic soils, and high temperature ceramics. Present JHM electrodes will melt or rapidly corrode under these conditions because of the locally higher temperature at the electrode.

The Joule heat source is more limited than the arc-plasma heat source so using a skull in a JHM is marginal. The INEL attempted to employ a high-temperature JHM for IEB waste form research and found more problems than solutions (see References 2 and 58).^c Arc or plasma-heated melters with transferred or nontransferred (arc to slag/melt) operation are capable of providing the intense heat source required without excessive electrode corrosion because the electrodes do not contact the melt or are of much higher temperature materials (e.g., graphite). The refractory corrosion problem can be overcome by using a water-cooled skull of the slag material between melt and reactor wall, while maintaining temperature with the intense heat source. Maintenance is related to graphite electrode consumption and replacement rates or to plasma torch electrode lifetimes.

The state of redox (reducing or oxidizing environment) is critical in the maintenance of some melters (as well as in obtaining optimum final waste form). Melters are designated as pyrolyzing with limited oxidation in the gas phase to vaporize and break down the organics with subsequent oxidation in an incinerator or afterburner. Oxidizing gas-phase melters are not treated explicitly, but could be substituted for combined melter and incinerator units. Oxidizing-slag melters are designed to oxidize metals in the melt/slag phase. Metal tapping melters allow the draining of liquid metal from the bottom of the metal melt, as well as slag from above it. Low-temperature JHM with Inconel electrodes work well under oxidizing or reducing conditions in the melt/slag or gas phases. A medium-temperature JHM with molybdenum electrodes will corrode rapidly under oxidizing conditions, but work satisfactorily under reducing conditions. The redox state in the gas phase of JHM does not appear to be a problem unless it influences the redox state in the melt/slag.

For arc melters, the use of graphite electrodes is no problem under reducing or neutral conditions. If the gas phase is oxidizing, the carbon will oxidize to CO₂. Coating the electrode with SiC or a similar substance has been shown to reduce the graphite oxidation. Flooding the electrode tip with argon can reduce oxidation of the tip. If air or nitrogen is present, undesirable levels of NO_x may be obtained in the offgas. This result appears to be melter dependent as well as operation dependent. Offgas treatment of NO_x is available, but should be avoided if possible. With graphite

c. G. A. Reimann, unfinished report on a small-size JHM operation, personal communication, 1991.

arc-melter operation, the melt/slag can be oxidizing if the oxygen getting into the gas phase is limited or its effect controlled, as above. A reducing slag is not a maintenance problem.

The allowed redox state for a plasma/arc melter with water-cooled metal electrodes can be more oxidizing than for the graphite-electrode transferred-arc melter. Both oxidizing and reducing states in either gas or melt phases are not problems, with the exception of air and NO_x as discussed above. With the graphite electrodes, the arc gap will probably be relatively short, with a small volume for NO_x production. With a plasma nontransferred torch, the plasma gas could be blown into the melt like an air or oxygen lance. If air, the nitrogen and oxygen will be effectively bubbled through the melt, the NO_x thereby quenched, and the NO_x generation could be increased. NO_x generation is, therefore, melter dependent. The NO_x generation at the MSE PAFE project⁵⁷ is less than expected^f considering the length of arc, the flow rate of air, and the intensity of the plasma. The maintenance of present plasma torch electrodes is expected to be more than on consumable graphite electrodes. The latter adds carbon to the melt which will change the Redox state and may diminish the quality of the waste form. Under chemical equilibrium, SiC is formed which may reduce the erosion at the refractory wall. In other plasma systems, electrode alloys have been developed to work in oxygen-rich environments (e.g., TiO_2 production). The next preliminary design phase needs to resolve differences between various melter features.

Questions which have arisen during this investigation regarding the processing steps in the SDS scenario are the following. Is it relatively convenient for the SDS Retrieval Subsystem to bypass or assimilate oversize objects without delays in overall processing? The system adds even more containers and other processing materials to the waste stream which may result in a volume increase. The addition of soil or other material for generation of the glassy/rocky final waste form was not delineated explicitly in the SDS and it is not known how this was to be done. (The modification presented here uses contaminated soil.) The Metals Decontamination Subsystem adds 40% more mass to the system than it treats. The same function can be performed in an appropriate melter with negligible addition of additional mass as discussed in Section 4.3. The packaging and assay for disposal presumes that appropriate assaying of the waste form will be available to assay TRUW monoliths in a size appropriate for disposal. This does not appear to be in accord with projections for assaying capabilities in the future. Also, there is no post-treatment (e.g., controlled cooling cycle) to ensure that the final waste form has the material microstructure to provide the maximum leach resistance for toxic, TRUW, and LLW substances. This is a low-cost option to obtain the best final waste form characteristics.

Scenarios II through IV address improvements in the SDS scenario to overcome the above deficiencies. Scenario V considers the option of using borosilicate glass as the vitrified waste form where possible.

4.2.3 The Simple Retrieval and Burden Soil Separation Scenario

Scenario II (see Figure 4-6) proposes a simpler overall system than the sophisticated SDS scenario. Table 4-1 shows that it does not use any of the SDS subsystems, at least as such, and that several different sorting options are considered for comparative purposes and are dependent upon future disposal decisions. A simpler retrieval subsystem is proposed based on temporary buildings being constructed over the pit(s) or series of trenches. The recontainerized input waste is then transported to a more permanent preprocessing and treatment hub. The Soils Processing Subsystem

^f S. T. Kujawa MSE, Inc. private communication, September 1991.

- Assumptions:
- 1) Credible assays(s) need to be performed.
 - 2) Combustibles will be one of the largest problems for processing.
 - 3) Iron Enriched Bauxite (IEB) is the final waste form.

Scenario II - Simple Retrieval - Over Under Burden Soil Separation

Figure 4-6. Scenario II-A - Combined Incineration and Melting System with Simple Retrieval and over/under burden soil separation from the treated waste stream. Option A - no sorting other than Special Case.

is not used in lieu of using the soil as the base for dissolving the waste streams with excess soil being treated in the same treatment subsystems. The Metals Decon Subsystem is not used because metals decontamination or total oxidation will be done in the melting process.

The simpler retrieval system separates special waste cases as above, separates the overburden soil which is probably the least contaminated, and possibly the underburden soil which may be significantly contaminated down to the lava basalt. The contaminated soil within the trenches or pits and surrounding the containers or other objects will be designated "entrained" soil and would be included with the waste stream. An initial assay of bulk objects identifies potential radioactive problems during retrieval. The details of such a system are beyond the scope of work and resources available at this time, but might be represented simplistically by temporary building(s) within which remotely operated front-end loaders feeding the buried containers and boxes into intermediate containers for transportation to the shredder/crushers contained in the more permanent processing building. (Such a retrieval system has recently been designed in more detail.)^g The Processing building would also contain all the treatment facilities, on-site labs, etc. It could have a terminal for transport of the waste form elsewhere or use an expired area building for reburial purposes.

The burden soil is used as needed to augment the dissolution of the waste streams in the best final waste form glassy/rocky state possible. The waste plus entrained soil plus specially processed Special Case materials are sized in a shredder/crusher to approximately 50 mm (2 in.) to promote reasonable assay, classifying, feeding, and treatment conditions. (The INEL/MSE plasma centrifugal reactor at Butte, Montana, handles up to 100 mm (4 in.) sizes without problems.) An on-line assay is then performed to verify radioactive content for safe operation.

All five options for sorting (and resultant treatment) of the input waste stream are included: (A) and (E) no sorting, (B) sorting combustibles only which includes organic-laden soil, (C) sorting combustibles from noncombustibles (including organic-free soil) from metals, and (D) sorting metals only as shown in Figures 4-6 to 4-10. Each sorting option requires different treatment systems which are a part of that option. The mixers in the treatment functions may be optional depending on the mixing capabilities of the melter chosen.

In Option A (see Figure 4-6), the waste and entrained soil are not sorted further. Soil and flux are added to obtain optimum waste form chemistry and fluidity, if needed. The melter must be a high-temperature, pyrolyzing-gas, oxidizing-slag melter to be able to melt basaltic soil, pyrolyze combustibles in the gas phase and metals in the melt/slag phase, as well as dissolve the noncombustibles into the slag. The pyrolyzed gases are completely oxidized in an afterburner. Few melters have demonstrated such capabilities with one notable exception.

The INEL/MSE Retech PCR melter at Butte has recently completed several RWMC feed runs simulating waste loadings for 1/3 to 1/1 ratios of metal to INEL basaltic soil and for a 1/6 mass ratio of combustibles with heating values ranging from 900 to 2000 BTU/lb. The metals and combustibles were combined with the soil as the input waste stream. After processing, essentially all the combustibles and metals were oxidized and the slag exhibited characteristics of being mostly crystallized (rocky), which is the preferred final waste form, not vitrified (glassy). Note that the combustibles were not only pyrolyzed but oxidized. The oxidation was apparently enhanced by the plasma torch gas penetrating the slag/melt like an air lance. Questions remain about the disposition of the HVPM and the Ce surrogate for the TRU Pu. Other melters that may be able to provide

g. G. C. Loomis, personal communication, EG&G Idaho, December 1991.

similar results are any arc-plasma melters which can pyrolyze or tolerate oxidizing conditions in the gas phase and produce it in the melt. Low-temperature glass melters and medium-temperature JHM are unacceptable for this role because they cannot melt the metals as required.

All options include the possibility of generating a slag frit or monolith depending on disposal option decisions. The frit can be made into small 10-15 mm (1/2 in.) pieces that can be properly assayed for type and extent of radioactivity, or into monoliths. Assaying will determine the appropriate TRUW, reclassified LLW (10-100 nCi/g), LLW, or Clean disposal options. If the frit option is decided upon, the TRUW frit can be fused or remelted for monolith packaging at 1200-1400°C, hence, a medium-temperature melter. The following heat treatment may require heating to 1000-1200°C depending on the recrystallization process to be used. The LLW waste frit would be either remelted or solidified by an approved, acceptable method. After fusing or remelting the frit, it should be cooled slowly or a specified controlled cooling cycle followed to obtain the optimum crystalline microstructure for maximum leach resistance.

All options route the offgas from the incinerator and melter(s) to a special offgas treatment facility that is designed to separate the HVPM and other toxic or radioactive substances. These processes will vary with pollutant and are to be determined elsewhere. It is proposed that the residue be evolved as a frit to be assayed for type and extent of radioactivity and then dissolved in a low-temperature BSG glass melter. The expected low quantity of material suggests that further separation of TRUW and LLW streams is inappropriate here. Very little TRUW is expected, so the waste is packaged for LLW disposal.

Option B (see Figure 4-7) is almost identical to Option A. The combustibles are sorted out and run into a thermal desorber (pyrolyzer) from whence the organics, the cemented/silicated organic bearing chunks, and the nitrate offgases (NOX and O₂) are fed to an incinerator, such as a rotary kiln. The thermal desorber may or may not be necessary depending on tests with heterogeneous compositions or subsequent findings. The smaller soil and cement particulates are routed to an oxidizing-slag, metal-tapping, high or medium temperature melter. Operating mode will depend on whether the metals can be surface oxidized or must be melted and oxidized. The choice will be determined by subsequent testing. Offgas may be routed to the incinerator or offgas treatment as necessary.

Option C (see Figure 4-8) is identical to Option B except that the waste stream is separated into combustibles, noncombustibles, and metals. The noncombustibles are dissolved into a nonoxidizing medium-temperature melter for improved maintenance. The metals are routed into a smaller high/medium-temperature, oxidizing-slag, metal-tapping melter with the same choices of operation as Option B.

Option D (see Figure 4-9) is also identical to Option B with the exception that only metals are sorted out of the waste stream (to the extent that is convenient). In practice, Option B may degenerate to Option D if it is difficult to separate soils with and without organics or chunk-sized construction materials from cemented/silicated organics. Option D may require a larger incinerator than Option B but a similar-sized melter because all the uncombusted material will end up in the melter. Again, the melter will operate at high or medium temperatures depending on whether surface-metal or total-metal oxidation is required. Figure 4-10 also illustrates the cryogenic fracture size reduction and air-liquifaction plant options. The air-liquifaction plant would provide both liquid nitrogen for cryogenic fracture and oxygen for combustion and oxidation.

Assumptions: 1) Credible analysis need to be performed.
2) Combustibles will be one of the largest problems for processing.
3) In-n Enriched Basalt (IEB) is the final waste form.

Scenario II - Simple Retrieval - Over Under Burden Soil Separation

Project No. 015522

Figure 4-7. Scenario II-B - Separated Incineration and Melting System with Simple Retrieval and over/under burden soil separation. Option B - Sorting combustibles only.

- Assumptions:
- 1) Credible assays need to be performed
 - 2) Combustibles will be one of the largest problems for processing
 - 3) Iron Enriched Basalt (IEB) is the final waste form

Scenario II - Simple Retrieval - Over Under Burden Soil Separation

Process No. 015525

Figure 4-8. Scenario II-C - Separated Incineration and Melting System with Simple Retrieval and over under burden soil separation. Option C - Sorting combustibles, noncombustibles (including entrained soil), and metals.

- Assumptions: 1.) Credible assay(s) need to be performed.
2.) Combustibles will be one of the larger problems for processing.
3.) Iron Enriched Basalt (IEB) is the final waste form.

Scenario II - Simple Retrieval - Over Under Burden Soil Separation

Project No. 015524

Figure 4-9. Scenario II-D - Separated Incineration and Melting System with Simple Retrieval and over/under burden soil separation. Option D - sorting metals only.

Option E (see Figure 4-10) is also identical to Option B with the exception that there is no sorting. In practice, Option B and D may degenerate to Option E if it is difficult to separate the various waste streams as indicated. Option E may require a slightly larger incinerator than Option B or D, but a similar-sized melter because all the uncombusted material will end up in the melter. Table 2-6 gives the masses of the material categories. Of the metals, the steel drums would go through the incinerator with their contents anyway. Special case materials, such as large machines, vehicles, etc. would not go through the incinerator. The noncombustible building materials are less than 10% of the other TRUW. The net added metal material required to go through the incinerator is probably about 30% more than in Option B. In addition, the incinerator will preheat these other materials via the incineration, thus reducing both the energy and the residence time required in the melter. The melter will operate at high or medium temperatures depending on whether surface-metal or total-metal oxidation is required. Figure 4-10 also illustrates the cryogenic fracture size reduction and air-liquifaction plant options. The air-liquifaction plant would provide both liquid nitrogen for cryogenic fracture and oxygen for combustion and oxidation.

A comparison of the sorting options A-E is given in Table 4-2. Relative quality points are assigned as indicated below the table and cover sorting, safety, maintenance and cost on a relative, but qualitative basis. Ten points are given if an option does not have an incinerator or second melter. The total number of points is close. The no sort, incinerator plus melter option (E) leads the way because of a combination of simplified sorting, control, safety and slag consistency. The metals only sort option (D) is second because of identical advantages, but requiring the additional metals sorting. The no sort Option A is third, mainly because of single unit operation plus no sorting. It falls behind Options E and D because of the more complicated melter control and maintenance required. These results are qualitative but do confirm concerns about the four options. Option E also has other advantages not considered in Table 4-2, such as reduced energy and residence time requirements.

4.2.4 The SDS Retrieval and Total Soil Separation Scenario

Scenario III (see Figure 4-11) is identical to Scenario II, but utilizes the SDS Retrieval Subsystem as discussed in the SDS Scenario I (see Table 4-1). The entrained, as well as the burden soil, is separated from the containerized and special-case waste streams. In Scenario III, the soil is used to provide the base material for dissolution of the nonsoil waste streams with the exception of the offgas treatment system (see Scenario II) that used BSG frit. Excess soil will be processed as a waste stream in the melter option selected.

4.2.5 The SDS Retrieval and Soils Processing Scenario

Scenario IV (see Figure 4-12) is identical to Scenario II, but utilizes both the SDS Retrieval Subsystem and the SDS Soils Processing Subsystem of the SDS Scenario I (see Table 4-1). Therefore, the total soil is separated from the containerized and special-case waste streams by the Retrieval Subsystem and the soils are then processed by the Soils Processing Subsystem. Special options are indicated on Figure 4-12 for this scenario. In Option K, the TRU-contaminated soil (plus any LLW soil needed) is used for the melter makeup soil; whereas, the LLW soil is solidified or packaged. This option would contaminate the nonsoil waste streams with TRU-contaminated soil, increasing its average contamination level. An alternative is Option L in which the small amount of TRU-contaminated soil is assayed for type and extent of radioactivity, then melted in a low-temperature BSG glass melter to minimize vaporization, and poured into monoliths for TRUW packaging and disposal. The LLW soil is used for makeup soil in the main waste stream melters. This will tend to dilute the TRUW effect. Option L appears to be the best choice here.

Figure 4-10. Scenario II-E - Separated Incineration and Melting System with Simple Retrieval and over/under burden soil separation. Option E - no sorting other than Special Case. Also includes cryogenic size reduction and the air liquifaction plant options.

Table 4-2. Comparison of input sorting Options A, B, C, D & E.^a

	A	B	C	D	E
			NonComb		
			Comb		
<u>Quality</u>	<u>None</u>	<u>Comb</u>	<u>Metal</u>	<u>Metal</u>	<u>None</u>
Sorting ease	10	6	4	8	10
Control of Incineration ^b	10	8	8	8	8
" " Melter 1	6	8	8	9	9
" " Melter 2 ^b	10	10	9	10	10
Slag consistency Melter 1	4	8	9	9	9
" " Melter 2	10	10	9	10	10
Safety of sorting	10	6	4	8	10
Safety of Incinerator	10	8	8	9	9
" " Melter 1	6	9	8	8	9
" " Melter 2	10	10	10	10	10
Maintenance of Incinerator	10	8	8	8	8
" " Melter 1	4	6	6	6	6
" " Melter 2	10	10	8	10	10
Cost of Incinerator	10	8	8	8	8
" " Melter 1	6	8	8	8	8
" " Melter 2	<u>10</u>	<u>10</u>	<u>10</u>	<u>10</u>	<u>10</u>
Quality Points	136	133	125	139	144

a. Relative quality points awarded on the basis of excellent-10, very good-8, good-6, fair-4, and poor-2.

b. If no separate incinerator or second melter, award is 10 points.

T. L. Eddy, B. D. Raivo

February 12, 1992

Thermal Processing Technologies - Conceptual Process Flowchart

- Assumptions: 1.) Credible assay(s) need to be performed.
 2.) Combustibles will be one of the largest problems for processing.
 3.) Iron Enriched Basalt (IEB) is the final waste form.
 4.) The SDS Retrieval Subsystem is used.

Figure 4-11. Scenario III - Scenario II options but including the SDS Retrieval Subsystem and total soil separation.

- 1.) Credible assay(s) need to be performed.
- 2.) Combustibles will be one of the largest problems for processing.
- 3.) Iron Enriched Pasalt (IEB) is the final waste form.
- 4.) The SDS Retrieval Subsystem is used.
- 5.) The SDS Soil Processing Subsystem is used.

Scenario IV - SPS Retrieval Subsystem, Total Soil Separation, SDS Soil Processing Subsystem

Figure 4-12. Scenario IV - Scenario II options but including the SDS Retrieval Subsystem, total soil separation, and the SDS Soil Processing Subsystem.

4.2.6 The Borosilicate Glass Scenario

Scenario V (see Figure 4-13) is similar to Scenario IV, but uses BSG as the makeup "soil" or glass material. Both the SDS Retrieval and Soils Processing subsystems are employed. The TRU-contaminated soil is processed as in Option L which was with BSG. Options A, B, C, D, and E then use BSG for makeup instead of INEL basaltic soil. The advantage of BSG is that lower-temperatures can be used in the melter while maintaining fluidity, but only as long as the waste streams do not have a high metallic content. A high metallic content converts a predominantly borosilicate glass into a predominantly iron-enriched basalt ceramic so that nothing is gained by using the BSG unless many times the waste stream mass is consumed. This would drastically increase the final waste form volume to many times the input waste volume which is an impractical solution.

In the IEB research, it was found that an average INEL TRUW could be combined with INEL soil in a 100/0 to a 0/100 ratio range and still make a high quality IEB final waste form (see References 2, 6).⁵⁸ It is, therefore, much more appropriate to use the available contaminated soil, that must also be treated, in the oxidizing-slag, metal-tapping, metal-processing melters at high temperature than attempting to use BSG in a medium-temperature melter, requiring several times the waste mass plus extensive flux to maintain fluidity. The only viable use for BSG is in the noncombustible waste stream melters of Option C. This option had the least number of quality points in Table 4-2 and represents one of the most complex options without obvious benefits. It appears that BSG will be most appropriately used for encapsulating special low-flow waste streams at low temperatures to discourage vaporization and yet provide a simple proven system.

4.2.7 Comparison of Scenarios and Options and Recommendations

The SDS Scenario I is used as a comparison base case and has been modified to meet more detailed requirements; hence, it is not a viable option. The Borosilicate Glass Scenario V has been shown to be impractical as a scenario because the final waste form will be a form of iron-enriched basalt unless a glass mass many times the waste mass is used. Scenarios II, III, and IV differ mainly in the use of (II) a simpler retrieval subsystem, (III) the SDS Retrieval Subsystem, and (IV) the SDS Retrieval and Soils Processing Subsystems. It is not known if the TRU Clean/Clear system of the SDS Soils Processing Subsystem will work. We know that the melters can process this soil effectively and therefore eliminate Scenario IV as viable. This also eliminates the need for Options L and K.

The main differences between Scenarios II and III are (a) the physical form of the retrieval subsystem and (b) whether the entrained soil will go with the waste stream or the soil stream. There appears to be about ten times as much soil in the entrained and burden soils as needed to assimilate the TRUW/LLW waste. The preferred sort/treatment option is Option E with an incinerator and melter, but no sorting. It, therefore, would be frugal to keep as much contaminated soil with the waste stream as possible to reduce sorting, handling, and potential contamination while providing the soil makeup needed for the melter(s).

The solution for the system design is becoming clearer. A simple retrieval system not necessarily unlike the SDS Retrieval Subsystem, routes all the potentially contaminated soil with the main waste stream. Size reduction and safety assay are followed by Option D (metals only sort) or possibly Option A or E (no sort). The recommended scenario is II-E presented in Figure 4-10.

Additional questions regarding the recommended Scenario II-E include the following. The thermal desorber may or may not be necessary. Tests with heterogeneous compositions or additional information from other sources need to be arranged. The operating mode of the melters will depend

- Assumptions:
- 1.) Credible assay(s) need to be performed.
 - 2.) Combustibles will be one of the largest problems for processing.
 - 3.) Borosilicate Glass is the final waste form.
 - 4.) The SDS Retrieval Subsystem is used.
 - 5.) The SDS Soil Processing Subsystem is used.

Scenario V - SDS Retrieval Subsystem, Total Soil Separation, SDS Soil Processing Subsystem, Borosilicate Glass Final Waste Form

Figure 4-13. Scenario V - Scenario II options but including the SDS Retrieval Subsystem, total soil separation, SDS Soil Processing Subsystem, and with a Borosilicate Glass final waste form.

on whether the metals can be properly surface oxidized to remove the TRU or must be totally melted and oxidized. This choice needs to be determined by subsequent testing. Assaying soil and frit should be reviewed or tested to determine limits of the assay. Other testing will be required to optimize processes in the melter.

4.3 Radiological Assays

As described earlier in this report, the buried mixed wastes and contaminated soils at the SDA represent a highly heterogeneous input waste stream for any treatment process. Although the bulk of the waste materials expected to be encountered have been generally identified, considerable uncertainty exists as to the exact quantities and distributions of these materials. These uncertainties are related to unknowns in original waste coding practices, the relatively lower accuracies used for initial waste assays, and the varied disposal practices of the times. Degradation of containers over time and further degradation likely during retrieval will further increase these uncertainties. The potential also exists for encountering some presently unidentified materials.

In order to achieve a safe, effective, and efficient process, the treatment process must be highly robust and accommodating to potential input material variations. The final waste form material must also be sufficiently uniform and measurable to categorize it for final disposition as LLW or TRU.^{59,h}

High uncertainties are associated with present radiological assay technology capabilities for TRU waste. As a result, measurements and controls used for process operations activities must include large margins to accommodate the degree of uncertainty. The uncertainties are associated with the heterogeneous nature of the waste matrix, the unknown radionuclide distribution, wide material density differences, materials self-shielding, and the short time available for examination in a production operation.

For the purposes of waste processing following retrieval of intact containers, it is generally felt that a good job of characterizing and assaying the waste "as is" can be done by existing analytical methods, by investing large amounts of time on a per container basis.⁶⁰ Using this approach to attempt processing a bulk rate of tons per day of retrieved materials, which will not necessarily be in intact containers, is clearly impractical.

Figure 4-14 illustrates various types of assays and their requirements across the processing spectrum. In the front end of the ex situ thermal processing system, an initial assay is assumed to be performed during retrieval operations (by others). This initial assay is viewed as likely having a very high uncertainty due to large uncertainties in existing assay technology relative to heterogeneous unknown waste materials and opportunities for error at higher throughput rates. Although some work is being done to develop improved radiological assay capability, the results are uncertain. The thermal processing system scenarios presented in this report outline methods intended to increase the credibilities (decrease uncertainties) of radionuclide assays required for process monitoring and control by lessening the degree of error in application of any assay technology associated with bulk processing. The process approach taken is to first place the waste in a physical form (by sizing) which will improve the accuracy and resolution of a bulk rate assay performed by any existing and forthcoming assay technology and, second, to assay several points both before and after the thermal

h. B. C. Anderson (Westinghouse Electric, WIPP), personal conversation, Regulatory trends and future requirements for rad-waste disposal sites.

Assay System Scenario

- Assumptions: 1.) Credible assay(s) need to be performed.
2.) Combustibles will be one of the largest problems for processing.
3.) Iron Enriched Basalt (IEB) is the final waste form.

Figure 4-14. Types of and requirements for radiological assays at various stages in the generic processing scenario.

processing steps and again after final packaging. On the input feed stream, bulk size reduction will lessen the measurement uncertainties tied to heterogeneity, radionuclide distribution, density, and self shielding. The extent of the required size reduction will depend on the degree of certainty obtainable from the selected/developed assay technology, but the realistic limit is viewed as being in the 1-2 cm range. The numbers obtained from the assays used for process monitoring and control purposes are to ensure safe and product effective processing operations. A final assay of the waste form is performed at the output of thermal processing operations, which will yield a further improved degree of credibility (e.g., homogeneous frit or monolith). This post processed assay is expected to provide the highest quality assay since the material will be very homogeneous by this point. It is further proposed to perform an assay for shipment purposes after packaging and just prior to shipment.

4.4 Processes in the Melter

Several processes are identified which affect the internal operation of the melter. In general, these processes can be categorized into three areas: physical processes in the melter, chemical processes in the melter, and the vitrification/devitrification processes in the final waste form. These three processes internal to the melter are interrelated to the production of the acceptable final waste form for final disposal. These processes are discussed below, along with aspects which need to be refined to improve operation of a treatment plant.

4.4.1 Physical Processes in the Melter

Relevant properties that influence physical processes internal to the melter and are required to be controlled within certain ranges include melt temperature, melt viscosity, melt corrosivity to the melter refractory materials, melt electrical conductivity, and the melt thermal conductivity.

Melt Temperature

The operational ceiling temperature of a melter is limited by the erosion of the electrode materials and melter configuration used. The ceiling temperature limits the melt formation temperature of a slag and subsequently the type of the waste form product produced, i.e., more durable high temperature glass-ceramics vs less durable low temperature glasses. The melt temperature has a direct effect on the volatilization of HVPM, but the loss will be dependent on transport by convective diffusion which is tied in with viscosity and its dependence on temperature and composition. The melt temperature can be effectively controlled by the addition of alkaline, alkaline earth, and boron oxides into the melt; but these materials can increase the leach rate and reduce the effective lifetime of the final waste form.

Melt Viscosity

The viscosity of the melt is inversely related to the melt temperatures. The viscosity of a slag melt at a certain temperature can be lowered by the addition of alkaline and alkaline earth oxides, boron oxide, and phosphoric pentoxide; or raised by the addition of high valency oxides such as SiO_2 , Al_2O_3 , TiO_2 , ZrO_2 , etc. Excessive addition of the latter oxides can freeze up a melt, requiring plasma melting or jack-hammer removal. A highly fluid alkaline slag melt is not too desirable because it will increase the rate of slag corrosion on the melter refractory materials as the slag moves against the refractories. A high alkaline slag is not too desirable either because the final waste form produced from this kind of slag will not be very leach resistant. Choosing a proper value of viscosity at a certain temperature is critical to pouring of the slag melt for casting as well as for producing an acceptable final waste form.

Melt Corrosivity To Melter Refractory Materials

The corrosiveness of a slag is a function of the alkaline oxide or phosphoric pentoside contents in the melt. The higher the contents of these materials, the more corrosion of the melt to the melter refractory materials. The corrosion increases when the melt becomes very fluid because the rate of interaction/reaction between the slag and the refractory interface increases. In order to prevent excessive corrosion of the melter refractory materials, the alkaline oxide or phosphoric pentoside contents in the melt should be critically controlled. The relative reactivity between slag and refractory can contribute to corrosion. The so-called acidic or basic nature of the slag and refractory compositions must be considered and the refractory must be chosen to minimize reactions for the typical slag composition. Convection near the slag-wall-atmosphere interface also increases the corrosion rate by increasing concentration gradients and mass transfer coefficients. Pilot study tests of different refractories under actual convective conditions should be made. Bench-scale validation of suitable newly-developed refractories should be initiated, similar to those on the prior INEL IEB research (see Reference 6). The corrosion resistance of graphite to an IEB melt as a function of temperatures should be tested.

Melt Electrical Conductivity

The melt electrical conductivity is directly proportional to the melt temperature. The slag conducts electricity through the cations and anions. In a slag melt containing a significant number of alkali ions, the transmission of electrical current is primarily due to alkali metals because the mobility of the monovalent alkaline ions is much higher than other bivalent metal ions. For this reason, the addition of alkaline ions into a slag melt at constant electric current will increase its electrical conductivity and lower the Joule heating effect in the melt. Consequently, the melt temperature will decrease. A loss or lowering of the Joule heating effect may cause freezing of the melt. The addition of bivalent metal ions, for example Ca, into a melt will only lower the melt viscosity but not the melt temperature (Joule heating effect) as long as alkaline ions are present.

Melt Thermal Conductance

The viscosity of a slag melt has strong influence on the thermal conductance within the melt. The thermal conductivity of the melt increases with increasing temperature because of the increased dielectric nature and mobility of cations and anions. The viscosity of the melt decreases with increasing temperature because of the gradual change from a solid to a liquid to give increased melt fluidity. The thermal gradients in the melt induce recirculation which homogenizes the melt composition, makes the temperature more uniform, and increases the diffusion-limited reaction rates within the slag. Thermal convection also increases with melt fluidity. The thermal conductance in the melt is a function of both conduction and convection, but is mainly influenced by convection at the higher temperatures. Modeling design studies should be initiated to determine appropriate melter geometries using available FIDAP finite difference and GPP slag chemistry codes.

4.4.2 Chemical Processes in the Melter

Relevant chemical processes which are internal to the melter and require attention include combustion and pyrolysis, disposition and influence of the halides, oxidation of metals, and slag-chemistry processes.

Combustion and Pyrolysis

The combustibles in the incoming waste stream are organic materials. They may be incinerated prior to entering the melter. Two operating modes could be used in the melter to handle the combustibles: pyrolysis (the vaporization and breaking down of complex organics) or oxidation by combustion. Pyrolysis has the advantage of minimizing and buffering any stronger combustion

reactions that might occur in the melter. The pyrolysis mode might create a reducing environment in the slag melt leading to potential metal (iron) partitioning from the slag (iron replaced by aluminum, chromium, etc. in the oxide). A reducing slag melt has the potential of volatilizing the HVPM from the melt, but most of them will be in oxide form and will not be reduced by any excess iron. In the oxidation mode, most of the combustibles would be oxidized in the melter, with the rest in an afterburner. The slag melt would be subjected to an oxidizing environment, oxidizing the metals. Oxygen could be supplied above the melt to assist oxidation, or delivered through the slag melt by a gas bubbler. The technology for delivering oxygen into a slag melt has been well developed in the pyrometallurgical industry. Potential volatilization of gas phase suboxides of the HVPM, e.g., lead suboxides, from the melter might occur, requiring offgas collection and treatment. The redox state of the melt influences or is an indication of volatilization of HVPM, slag and ultimate waste form chemistry, and the stage of process development. The extent of and location of combustion and pyrolysis will influence the redox state in the melt.

Disposition and Influence of Halides

The disposition of halides, particularly chlorides, can be important. Chlorides in the melt will lower melting points, thus increasing volatilization of the HVPM. Most of the halides will be directed to the offgas system where they will be collected, whether via an incinerator or melter oxidation. Some chlorides will end up in the melt. Their effect needs to be checked to determine its significance. Monitors could be installed on the melter system to notify operators when excessive amounts are in the slag so corrective action (e.g., adding TRU-contaminated soil) can be taken.

Oxidation of Metals

Metal decontamination can occur via surface oxidation of the contaminated metals. The oxidation of metals can be considered from either the surface oxidation or the total oxidation scenarios. In the surface oxidation scenario, the metals contaminated with TRUs would enter the slag/melt bath, the TRUs would be dissolved into the slag melt with the surface metal oxidation, and the decontaminated metal would then be dredged or melted and tapped. In this case, the melter would be required to operate at a near-neutral oxidizing condition. The melt temperature may not be as high as the melting temperature of the metal, if dredging is used. Surface oxidation of metals may not be easy to both control and handle without preliminary studies to determine the efficiency of the process, identifying problem areas to be overcome, and developing criteria for sizing, agitation, and other procedures. Bench-scale studies of metal surface oxidation to indicate proof of principle are needed. Concentrated studies in the pilot plant would be needed to consider the effects of the melter configuration, convection, metal orientation, the need for bubbling, etc. on the actual surface oxidation efficiency.

In the total oxidation scenario, the metal would be completely oxidized and dissolved in the melt with additional oxygen delivered into the melt to assist oxidation. To hasten oxidation, the metal dimensions need to be reduced and the melt agitated by bubbling, electromagnetic stirring, or equivalent. Total metal oxidation may be an important problem because, if required, it may lengthen the residence time to undesirable periods. Bench-scale studies should be initiated in concert with surface oxidation to determine methods to reduce the potential residence time without adversely affecting the other desired properties of the slag melt.

Slag-Chemistry Processes

The slag-chemistry process is the most important part of the melter operation because it deals directly with the fabrication of the final waste form and its performance characteristics. There are several important parameters to be considered in the fabrication of an acceptable high integrity final waste form as follows:

- Retention of HVPMs in the slag. It is desirable that the volatilization of the HVPM be minimized even at high temperatures. Any vaporized metals or metal oxides would condense and be collected as particulates in the offgas treatment system. Retaining them in the slag would simplify the process. The volatilization of the HVPM is closely related to the redox state and the temperature of the melt. The incorporation of the HVPM into the slag would be enhanced if the melter is operated under oxidizing conditions. Tailoring the slag chemistry to produce high temperature ceramic phases which can dissolve the HVPM such as Pb, Zn, Cd, etc. to form stable compounds or solid solutions is highly desirable. Bench-scale tailored-design studies of the slag chemistry should be focused in this direction to maximize the retention of HVPM in the slag.
- Retention of TRU radionuclides in the slag. The slag melt must be able to dissolve the TRUs and incorporate them in its matrix. The TRU metals are extremely reactive and would form oxide compounds or oxide solid solutions with alumina, titania, and zirconia to produce mineralogical hollandite, perovskite, and zirconolite phases. These phases occur in Synroc, a hot isostatic pressing (HIPING) process at modest temperatures, and have demonstrated excellent product performance characteristics. Tailoring the slag chemistry to produce these high temperature crystalline phases which will retain the TRU species in an IEB matrix are highly desirable. Detailed tailored design studies on the slag chemistry should be focused on methods to improve the retention of TRUs in the IEB4, $\text{ZrO}_2/\text{TiO}_2$ modified IEB, type of slag. Bench-scale studies with rare-earth lanthanides as surrogates for the TRUs should be initiated at the INEL Research Center (IRC), as well as specific tests with TRU at Test Area North (TAN).
- Retention of LL radionuclides in the slag. The slag-chemistry condition to capture the LL in a slag is similar to those of the TRUs. Rare-earth lanthanides may not be the proper surrogates for the LL. Nonradioactive isotopes of the LL could be used in the tailored slag-chemistry investigations. IEB4 is also expected to be an excellent matrix for LL retention. IRC bench-scale tests for TRUW and LLW simulated wastes should be performed concurrently. Bench-scale tests concurrent with TRU-retention tests at the site should be performed to prove and confirm the less expensive surrogate experiments.

Some experiments have been performed on the volatility of Cs from the melters. In prior IEB research at the INEL, cesium oxide was expected to evaporate from the melt at a rapid rate, but this was shown not to be true [see Reference 6]. Some of the cesium remained in the slag and some evaporated. The conditions to retain the Cs in the slag need to be investigated with nonradioactive Cs as an ideal surrogate. Experiments with Cs will probably indicate the mechanisms to retain other HVPM as well or indicate that it is impractical. This subject warrants further work.

- Redox State of the Melt. The ratios of $\text{FeO}/\text{Fe}_2\text{O}_3$ (or $\text{Fe}^{2+}/\text{Fe}^{3+}$ cations) in the slag indicate the redox state of the melt. The ratios of $\text{Fe}^{2+}/\text{Fe}^{3+}$ cations are optimal between 0.1 - 0.5 in terms of avoiding undesirable unstable foaming and precipitation of metallic species during processing. Tailored design studies on proper conditions of the redox state in the melt may be applied to generate a high density and high viscosity slag foam to capture escaping HVPM at high temperatures. The redox state appears to be related to many of the results from materials characterization of mineral (glass and ceramic) states including recrystallization temperatures. Its value may be used as a

gauge to meter the formation process of the desired waste form. Other studies should include determination of the redox state of the melt to provide a base of information from which to determine if a focussed study relating redox state to final waste form characteristics and processing conditions is warranted.

- Electrode corrosion and erosion. The melter operation scenario could involve oxidizing or reducing environments. The interaction of the electrode material, e.g., graphite or copper, with oxygen would create a serious corrosion problem. Other chemical reactions may occur due to the complex composition of the off gases. Metal alloys have been developed for electrodes operating in pure oxygen. Graphite electrodes with SiC coatings have been developed to minimize oxidation of the graphite. Electrode erosion can also be a problem if high current loading of the electrodes occurs. Metal electrodes used in high erosion applications usually employ thick dimensions to lengthen lifetime. Graphite electrodes in the scrap melter/smelter industry are consumable electrodes which are advanced as they are used up. The decision as to which type of electrodes and melter configuration should be determined in Phase II of the SDS. Bench-scale test results and/or existing vendor experimental data should be obtained to provide explicit information on electrode corrosion with IEB slag.

4.4.3 Vitrification/Devitrification Processes in Slag

There is a great deal of evidence that leach resistance can be increased by crystallizing the slag as it cools into the final waste form. The crystals are usually more leach resistant. Recrystallization or devitrification occurs at different temperatures for different minerals, and hence over the temperature-time cooling curve. The minerals have different composition than the bulk material; therefore, the remaining glass is depleted of the elements in the crystals and the remaining elements increase in composition in the glass. The alkalis are usually not part of the crystals that form at the higher temperatures. They are found in the relatively low temperature feldspars and some pyroxenes which form in the last stages of solidification. If the slag is cooled quickly, the alkali-containing crystals do not form and the alkalis are in the vitrified, amorphous glass. The alkali glass is also more easily leached than the crystalline structure and deteriorates the structure as a whole over time. The deterioration increases the surface area of the crystalline material, thus decreasing its leach resistance.

Slow cooling of the slag produces predominantly crystalline phases including the feldspars and pyroxenes containing alkalis. A variable cooling and possibly heating schedule has been used to first nucleate and then grow desired crystals on a limited basis. Controlled cooling would, therefore, allow a manipulation of the vitrification and devitrification processes in the slag to produce the desirable durable ceramic phases with an engineered grain size. These controlled cooling processes have been shown to produce a final waste form with much superior product performance characteristics than many other waste forms (see Reference 6).⁶¹ Prior experiments on controlled cooling demonstrated proof of concept and just started parametric studies to optimize the cooling profile with time. Experiments to determine nucleation temperatures for desired mineral phases and cooling profiles for IEB/IEB4 compositions to become an approved waste form for TRUW are needed.

4.5 R&D to Optimize the Waste Form and Processes

The present state of the art in rotary-kiln incineration and plasma-heated melters is such that a treatment facility for demonstration and subsequent operation could be designed today and operated in the near future. The various feasibility and more advanced design studies have identified

appropriate methods for site classification, retrieval, treatment, assaying, packaging, and a good waste form. Material handling, incinerator, and offgas treatment systems are now available.

The waste management R&D performed over the past 15 years has contributed to and resulted in this conclusion. The research results on the IEB waste form are no small contribution and have set the stage of confidence in the waste form and how to make it. Pit 9 has been sufficiently characterized. Retrieval methods have been appropriately simplified. Several waste stream sizing methods are available. Complex sorting methods are unnecessary. Containment methods are being finalized. Incineration methods for mixed LLW were developed and operated at Process Experimental Pilot Plant (PREPP) and Waste Experimental Reduction Facility (WERF). Plasma-heated melters have successfully made very leach resistant waste forms from feeds spanning the range from INEL soil (A-100) to soil with much metal and organic material (A-40). TRAMPAC containers have been designed and tested.

Further studies can improve many aspects of the system, including the quality of the waste form and the overall efficiency of the handling and treatment processes for making that waste form. These studies would run parallel to the next preliminary design phase focussed on the specific type of components to be installed. Topics for additional R&D to optimize the system and waste form, as well as proposed testing, follow.

4.5.1 Recommended R&D and Priorities

The purpose of this section is to identify valuable R&D areas in high-temperature melter processing of the RWMC buried mixed TRUW. These topics are intrinsic to the melter processes and will have important consequences for the final waste form product performance characteristics. Laboratory-scale tests are needed to provide solutions to these problems and to generate guidelines for optimizing pilot-scale design and tests. Environmental, health, and safety constraints only allow bench-scale non-radioactive surrogate tests at IRC. Simulated surrogate tests will portrair possible scenarios for real TRUW conditions. It will be necessary to perform TRUW bench tests at the Site or elsewhere to investigate or confirm these scenarios. Other possible constraints are available facilities and manpower.

Several questions have been identified that are in need of research and development work. The listing of the topics is random and does not reflect any chronological order of importance. However, these topics are coupled (attempts to understand one topic need to consider the others) as follows:

- Dissolution and retention of HVPm in the slag melt
- Dissolution and retention of TRU and LL in the slag melt
- Refractory corrosion in the melter
- Combustibles and redox state in the melter
- Metal dissolution and oxidation
- Electrode corrosion and erosion
- Volatility of Cs from the melter.

Initial first series tests have begun to address some of these concerns. Tests have been conducted at PEC for plasma jet melting of INEL soil spiked with HVPms, at MSE for the plasma-arc centrifugal-reactor melting of INEL soil and simulated RWMC wastes, and at PNL for crucible melt tests of pure INEL soil with 74X simulated waste streams.

The nature of the various topics have been discussed above. Future bench-scale research and development work is discussed below.

4.5.2 Proposed Testing

HVPM - Tailoring the slag chemistry to produce high temperature ceramic phases which can dissolve the HVPM such as Pb, Zn, Cr, Cd, etc. to form stable compounds or solid solutions are highly desirable. IRC bench-scale tailoring design studies on the slag chemistry should be focused in this direction to enable the retention of HVPM in the slag.

Dissolution and retention of TRU and LL in the slag melt - Tailoring the slag chemistry to produce the high temperature ZrO_2 or TiO_2 IEB4 phases, which will retain the TRU species in stable compounds or solid solutions in an IEB matrix, are highly desirable. Bench-scale tailoring design studies on the slag chemistry should be focused in this direction to enable the retention of TRU in the slag. Bench scale with rare-earth lanthanides as surrogates for the TRU should be initiated. TRU bench-scale tests should be performed to prove and confirm the surrogate experiments. IEB4 is also expected to be an excellent matrix for LL retention. Bench-scale tests for TRUW and LLW simulated wastes should be performed concurrently.

Refractory corrosion in the melter - The corrosion resistance of graphite or carbide crucibles to an IEB melt should be tested at different temperatures. Bench-scale validation of suitable newly-developed refractories should be initiated, similar to those on the prior INEL IEB research (see Reference 6).

Combustibles and redox state in the melter - Bench-scale tailored design studies should be focused on the proper conditions of the redox state in the melt to generate a high density and high viscosity slag foam to capture escaping HVPM at high temperatures. Other studies should include determination of the redox state of the melt to provide a base of information from which to determine if a focussed study relating redox state to final waste form characteristics and processing conditions is warranted.

Metal dissolution and oxidation - Bench-scale studies of metal surface oxidation to indicate proof of principle are needed. Lab studies could simulate the pilot plant melter to consider the effects of the melter configuration, convection, metal orientation, the need for bubbling, etc. on the actual surface oxidation efficiency. Bench-scale studies should be initiated in concert with surface oxidation to determine methods to reduce the potential residence time without adversely affecting the other desired properties of the slag melt. Bench-scale tests on metal oxidation should focus on its relation to the redox state of the melt and product phases formation.

Electrode corrosion and erosion - Bench-scale studies should focus on surface protection of the electrode and the electrode tip geometry on high current erosion. Bench-scale studies and existing vendor experimental data should be obtained to provide explicit information on electrode corrosion with IEB type of slag.

Volatility of Cs from the melter - The high retention of Cs in IEB at high temperatures contradicts the conventional expected behavior of Cs. Bench-scale studies should focus on the volatility of Cs with other oxides as a function of temperature to either confirm or deny previous results. Experiments with Cs will probably indicate the mechanisms to retain other HVPM as well as indicate that it is impractical.

Melter modeling studies - Modeling design studies should be initiated to determine appropriate melter geometries using available FIDAP finite difference and GPP slag chemistry codes.

Controlled Cooling - Prior experiments on controlled cooling demonstrated proof of concept and just started parametric studies to optimize the cooling profile with time. Experiments to determine nucleation temperatures for desired mineral phases and cooling profiles for IEB/IEB4 compositions to become an approved waste form for TRUW should be performed.

4.5.3 Potential Collaborators to Solve Problems

A number of university, National laboratory, and commercial/industrial collaborators are available for collaboration to solve problems. Some of them are listed in Table 4-3.

Table 4-3. Potential researchers and collaborators to solve problems.

<u>Vendors</u>	<u>Government/National Laboratories</u>
<u>JHM</u>	Bureau of Mines-Albany/ASME
Glasstech	INEL/EG&G S&T
Penberthy	INEL/EG&G Site
	INEL/MSE
<u>AHM</u>	INEL/WINCO CCP
Electromelt	LLNL-Molten Salt
Electrolysis Inc.	Los Alamos
Elkem Technology	PNL-Battelle
	SRL-Westinghouse
<u>PHM</u>	
Retech	<u>Universities</u>
Plasma Energy Corporation	Colorado School of Mines
<u>Cupola</u>	M.I.T.
Westinghouse	SUNY-Buffalo
Scorpion Mfg.	U. Idaho
	U. Missouri-Rolla
<u>Other</u>	U. Minnesota
Hazen Associates	U. Utah
SAIC-WTMD	

5. FIRST TEST SERIES RESULTS

5.1 Review of the First Test Series

The First Test Series is a number of experiments involving melters and/or melting from which information can be gleaned. The tests include the following.

1. PEC Test: Plasma heated melting of INEL soil and metal nitrates in a stationary melter pot using a nontransferred (plasma) torch at the Plasma Energy Corporation (PEC) facility.
2. ACT Test: Arc heated melting of INEL soil and diesel fuel in a centrifugally rotating melter pot using a transferred (arc) torch at the INEL/MSE Component Development Integration Facility (CDIF) as a afterburner component test (ACT).
3. RWMC Test: Similar to the ACT test but with variations of simulated RWMC feeds including metals, combustibles, HVPM (Pb), and TRU (Ce).
4. PNL Test: Similar to the RWMC Test, but under JHM conditions, performed in externally-heated crucibles and with alkali flux to obtain fluidity at lower temperatures.

Tests 1-3 were initiated prior to this work and Test 4 was a part of this work. A Melter Shakedown Test was devised for quick proof of whether existing JHM and PHM could melt or process INEL soil and TRUW. The RWMC and PNL tests are related to the Melter Shakedown Test procedures. The RWMC test processed all options without problems. The PNL Tests are still not complete, but have demonstrated the difficulty in processing metals and INEL soil in low or medium temperature melters (900-1500°C).

5.2 Melter Shakedown Tests

Several major questions were raised about melter capabilities to process INEL soil and TRUW. These questions were initially addressed in some First Test Series experiments. It is a popularly conveyed concept that JHM technology for waste treatment is state-of-the-art with numerous vendors with JHM (and processing techniques) sitting on the shelf awaiting purchasers. Plasma-heated melter technology, on the contrary, is believed to be new and in a research and development stage in spite of the fact that electric-arc furnaces have been smelting and melting metals and controlling slags for decades.

The first Melter Tests set up were to test existing melter technologies against their claims, e.g., proof of principle type tests. It proposed six simple tests that could be run at the vendors facility or at an installation or lab. Measurements only included power and mass data and slag temperature under operating conditions. Slag samples were to be returned to INEL/EG&G Idaho, Inc., for materials characterization. The six tests simulated RWMC TRUW and were to answer the simple questions:

- Can you melt INEL basaltic soil to fluidity without flux?
- Can you melt INEL basaltic soil with flux? How much is required?
- Can you melt soil and metals with flux?
- Can you melt soil and metal oxides with flux?

- Can you melt soil and metal oxides and HVPM with flux?
- Can you melt soil and metal oxides and treat organics with flux?

The metals and organics concentrations were analogs of the INEL/MSE RWMC feed tests at the CDIF for comparative purposes.

The results of requests for the PHM tests are the following. The RWMC Test ran both metals and organics at the same time, oxidized both, and yielded the desired predominantly-crystalline final waste form. No flux was required. The disposition of the HVPM is unknown at this stage of evaluation, but indications are that the lead was both vaporized and retained in the glass matrix of the waste form. The ACT Test results were similar, but yielded a larger fraction of glass phase than the RWMC Test. The PEC Test had previously run INEL soil plus metal nitrates in a PHM with and without alkali flux. The metal nitrates apparently vaporized near the beginning of the test, possibly during feeding, but the waste form was predominantly vitreous (glassy) phase with the chromium locked in the crystalline (rocky) phase.

The requests for JHM tests were met with no takers. In the first place, few JHM vendors are actually available. Those that are available operate predominantly in the low temperature range (900-1200°C), and to develop an appropriate medium or high temperature melter would require an extensive and expensive R&D program. PNL indicated that tests in existing BSG JHM would need to be in large JHM at mass rates of 1000 kg/day (2200 lb/day). Small JHM will not give a good indication of performance because the current stream lines and proximities of the cold walls do not scale. The basaltic soil presented a new challenge and could not be done without a considerable amount of flux (10-30%). The variable compositions presented fluidity problems in establishing reliable operating points without the danger of freezing up the melter. The high concentrations of metals were to be excluded from the tests for similar reasons plus the unoxidized metal in the bath could short out the current path. PNL proposed to do a set of crucible tests to identify operating ranges as a function of composition and temperature. After this R&D effort, a pilot plant could be designed and constructed to perform the melter tests requested. Other JHM vendors were concerned about the impact of the chunks of waste materials on stirring impellers and required marble-sized particles.

It appears that the PHM have no problem melting the TRUW, LLW, and soil; are extremely robust for variable input feed compositions such as found at RWMC/SDA; and can operate under oxidizing or reducing conditions, but need to be investigated for the treatment and disposition of the HVPM. The JHM are not at the stage of development needed for stabilizing the particular RWMC TRUW/LLW waste streams and considerable development of processes, electrode materials, and refractories, as well as improved sorting and control procedures for the waste stream are required. For additional information see Reference 3.

5.3 Scientific Experiments

Several tests have been initiated or monitored to evaluate the final waste form characteristics. WTDD initiated the melting of INEL soil and metal nitrates in a Plasma Energy Corporation (PEC) PHM with a nontransferred nitrogen plasma torch in a water-cooled tiltable melter. After initial heating, the soil and nitrates were fed into the melter through the torch plasma. After melting, the slag was poured onto a bed of sand and cooled over a period of 1-2 hours. As a result of this rapid cooling, the microstructure is quite fine with small crystals and dendrites distributed throughout the predominantly glass matrix. The zinc is found in the dendrite crystals which are probably pyroxenes.

The chromium is found in the pyroxene dendrites and as chromite. The alkalis (Na & K) are in the (aluminosilicate) glass phase, and the alkali earths (Ca & Mg) are in the glass phase and the dendrites. Leach tests and composition measurements indicated that little of the metals in the added nitrates remained in the slag. Nitrate decomposition temperatures are quite low (around 500°C) so that they may have been decomposed at the beginning.

The ACT and RWMC Test experiments are performed in a Retech Plasma centrifugal reactor with a transferred torch operating on air. Oxygen is provided through a tube in the gas phase. The first slag samples received were from the ACT Series afterburner shakedown tests which melted INEL basaltic soil and 10% diesel fuel. The waste form resembled black obsidian rock and was predominantly the glassy, vitrified phase with large concentrations of crystals and dendrites throughout the samples. The crystal orientation indicated flow or cooling patterns. The crystals were predominantly ferritic spinel with some chromite and the alkalis were absent, except in the alumina silicate glass matrix.

The RWMC Test series gave different results. This series had 3/1 and 1/1 metals to soil content plus wood chips and diesel fuel as combustibles. The combustibles were almost totally oxidized before reaching the afterburner and the metals were almost completely oxidized in the slag via the plasma-torch air lance. XRD measurements did identify a very small amount of free iron in the slag samples. The slag core samples indicated a predominantly crystalline (rocky) phase with some glass phase. The slag is cooled in the pig in the bottom of the reactor chamber for a day and then further cooled in ambient air, taking another day to cool to room temperature. This slow two-stage cooling process resulted in larger crystal formation than in the quickly cooled PEC tests. Also the large amount of metal and resulting metal oxide in the slag apparently increased the crystalline content drastically.

Figure 5-1 shows typical micro-photographs of the PEC, ACT, and RWMC with a magnification of 1000. The crystals in the ACT photograph are approximately 10-micron squares. A comparison of the photographs emphasizes the shift from a predominantly glassy (PEC test) to a predominantly crystalline (RWMC test) waste form.

The PNL Test results are not yet available for inclusion in this report.

It appears relatively easy to get excellent waste forms from plasma-heated melters.

PEC PLASMA MELTER TEST

- 0 INEL SOIL + NITRATES
- 0 RAPIDLY COOLED
- 0 MEETS TCLP REQUIREMENTS

MSE PAF ACT TESTS

- 0 INEL SOIL + DIESEL FUEL
- 0 SLOW COOLED
- 0 HALF GLASS & HALF CERAMIC
(CERAMIC = CRYSTALLINE)
- 0 LOW LEACHING

MSE PAF RWMC TESTS

- 0 INEL SOIL + STAINLESS STEEL,
DIESEL FUEL, WOOD CHIPS, & LEAD
- 0 SLOWLY COOLED
- 0 MOSTLY CERAMIC
- 0 LOWEST LEACHING

Figure 5-1. Microphotographs of the slag waste form from the PEC, ACT, and RWMC tests (1000X). The PEC slag is predominantly amorphous glass. The RWMC slag is predominantly crystalline rock.

6. CONCLUSIONS AND RECOMMENDATIONS

6.1 Input Waste Streams

The TRUW streams from the SDA at the RWMC are predominantly metals, organics in a variety of forms, materials made up of metal oxides, and a considerable amount of contaminated soil. Both toxic and radioactive substances are distributed throughout this heterogeneous mixture. There will be more than ample contaminated soil to stabilize the TRUW, as well as the LLW and toxic materials into a waste form with high leach resistance, long-range chemical and physical stability. Based on this preliminary analysis, the best way to do this safely, simply, efficiently, and with optimum control of the quality of the final waste form is as follows. Size the input waste for an on-line safety assay and downstream processing. Sort out the metals from the waste and contaminated soil stream for processing in an oxidizing-slag, high-temperature plasma/arc heated melter. The other waste and soil would be thermally desorbed to pyrolyze gases for the incinerator with the solid materials routed to the melter. The melter slag could be fritted, assayed to separate TRUW and LLW with the TRUW form being fused, packaged, and transported to WIPP, or an equivalent. Alternately, if the TRU level is below 100 nCi/g, the blended TRUW/LLW waste form could be packaged for reburial. HVPM that escape the slag will be collected and dissolved in a low-temperature Joule-heated melter with a BSG waste form.

6.2 Final Waste Forms

It has been determined that borosilicate glass is an inappropriate waste form for the high-metal and basaltic-soil contents in RWMC buried wastes. The low waste loadings required to force feed BSG would result in a significant increase in final waste volume instead of reduction. The few applications in which BSG could be used would require additional development costs and more complex sorting, waste stream composition control, and melter control systems which outweigh the benefits. It has also been demonstrated that JHM operation at high-temperatures is not state of the art and much development of the JHM itself would be needed. The same is not true of Plasma/arc-heated melters which have already demonstrated the fabrication of a desirable waste form from RWMC types of waste streams. The R&D can then focus on the refinement of the processes utilizing state of the art components.

6.3 Processing Systems

The recommended processing system scenarios is Scenario II, Option E (see Figure 4-10); it has the highest priority because it has no sorting (excluding special case sorting), the simplest control of incinerator and melter, only one melter, and maximum safety and maintenance.

It requires a less complicated retrieval system (already being designed by others) than the SDS Retrieval Subsystem that sorts out overburden soil which may be clean and passes nonspecial-case waste and other soil to the sizing crusher/shredder (<50 mm or 2 in.) and an intermediate assay for safety. The no-sort waste stream is routed to a thermal desorber with the pyrolyzed gases going to the incinerator and the solids going, with the metals, to a high temperature, oxidizing-slag, plasma/arc-heated melter. The metals may be surface oxidized, melted and tapped from the bottom of the melter, or totally oxidized and dissolved into the slag. Any combustibles getting to the melter will be at least partially oxidized and routed to the incinerator or offgas treatment system as appropriate.

If Option X (separate TRUW disposal) is selected, the output slag could be fritted to a size amenable to an assay to separate TRUW and LLW. It has been shown that a water quench may become contaminated under these conditions, requiring treatment. The TRUW frit can then be remelted or fused, heat treated to obtain the optimum final waste form, and poured into appropriate packaging. If Option Y (rebury blended TRUW/LLW) is selected, the slag could be poured into a monolith in the final packaging and controlled cooling used to obtain the optimum final waste form.

The melter processes need to be tested to determine how to minimize HVPM carryover, including TRU and LL radionuclides. Oxidation, followed by diffusion of the HVPM through a thick slag or foaming layer should reduce the loss into the offgas significantly. Any volatilized toxic or radioactive materials will be collected in the offgas treatment, assayed, dissolved in BSG in a low-temperature Joule-heated melter, and packaged for disposal. Offgas collection may be by condensation/solidification or other specific process (e.g., for Hg). These are to be determined for specific materials later.

6.4 Recommended R&D

Irrespective of the melter type, the following topics must be addressed in the near future for proper completion of the pilot plant tests:

- Crucible tests of the disposition of HVPM and metal oxides in high-temperature (1500-1800°C) processing. This should include As, Cs, Cd, Hg, Pb, and Zn.
- Crucible and melter tests of the retention and dissolution of TRUW and reconfirmation of uranium in zirconia-augmented slags.
- Crucible and melter tests to study metal oxidation and dissolution in the melter in both surface and total oxidation modes. The removal of TRU and LL radionuclides from the surface of metal artifacts would be a major aspect of this topic.
- Melter tests to confirm refractory/skull corrosion effects.
- Melter tests to confirm expected electrode corrosion/erosion effects.
- The redox state in the slag and its influence on the HVPM, as well as controlled cooling processes and their influence on the phase composition of the final waste form.

7. REFERENCES

1. J. L. Mayberry, W. J. Quapp, F. Feizollahi, J. C. Del Signore, and J. McFee, *Preliminary Systems Design Study Assessment Report*, EGG-WTD-9594, June 1991.
2. G. A. Reiman, J. D. Grandy, and T. L. Eddy, *Survey of INEL Research on the Iron-Enriched Basalt Waste Form*, EGG-WTD-10056, January 1992.
3. A. D. Donaldson, R. J. Carpenedo and G. L. Anderson, *Melter Needs Development Assessment*, EGG-WTD-9911, January 1992.
4. M. J. Vigil, *Subsurface Disposal Area (SDA) Waste Identification*, EGG-WM-8727, January 1990.
5. *Handbook of Chemistry and Physics*, The Chemical Rubber Co., 52nd Ed., Cleveland, OH, 1972-72.
6. J. E. Flinn, P. V. Kelsey, R. L. Tallman, S. P. Henslee, and W. C. Seymour, *Annual Report on the TRU Waste Form Studies with Special Reference to Iron-Enriched Synthetic Basalt*, EGG-FM-5366, 1980.
7. W. McCulla et al., "Treatment of Hazardous Wastes Using Wet Air Plasma Oxidation," *1st INEL Workshop on Plasma Applications to Waste Treatment, Idaho Falls, ID, January 16-17, 1991*.
8. M. J. Kirshner, "The Use of Combined Plasma Photolysis in the Treatment of Flue Gases," *1st INEL Workshop on Plasma Applications to Waste Treatment, Idaho Falls, ID, January 16-17, 1991*.
9. W. C. Neely and E. J. Clothiaux, "Decomposition of Organic Compounds by Silent Discharge Plasma," *1st INEL Workshop on Plasma Applications to Waste Treatment, Idaho Falls, ID, January 16-17, 1991*.
10. A. Czernichowski and H. Lesueur, "Multi-Electrodes High Pressure Gliding Arcs Reactor and Applications for Waste Gas and Vapor Incineration," *1st INEL Workshop on Plasma Applications to Waste Treatment, Idaho Falls, ID, January 16-17, 1991*.
11. D. Dalton, E. M. Steverson, and G. L. Anderson, *Air Pollution Control in Thermal Treatment*, EGG-WTD-10038, January 1992.
12. F. E. Flinn, P. V. Kelsey, Jr., R. L. Tallman, S. P. Henslee, and W. C. Seymour, *Iron-Rich Basalt-Type Waste Forms for Transuranic and Low-Level Waste Containment: Evaluation of Electromelt Casting*, EGG-FM-5241, April 1980.
13. K. D. Reeve, D. M. Lrvins, J. L. Woolfrey, and E. J. Ramm, Adv. in Ceram. Vol 8, *Nuclear Waste Management*, eds. G. G. Wicks and W. A. Ross, 1984, p. 200.
14. M. I. Goldman, J. A. Servizi, R. S. Daniels, T. H. Y. Tebbutt, R. T. Burns, and R. A. Lauderdale, Proc. 2nd UN Conf. on Peaceful Uses of Atomic Energy Geneva, 1958, Vol 18, p. 27.

15. R. Eliassen and M. I. Goldman, *Hearings on Industrial Radioactive Waste Disposal*, ed. R. C. Doan, 1959, Vol 3, p. 1966-1979, U.S. Govt. Printing Office, Washington, DC.
16. C. A. Mawson, *Management of Radioactive Wastes*, Van Nostrand, Princeton, NJ, 1965, p. 196.
17. J. L. McElroy, W. J. Bjorklund, and W. F. Bonner, *The Treatment and Handling of Radioactive Wastes*, eds. A. G. Blasewitz, J. M. Davis and M. R. Smith, Springer, New York, 1982, p. 171.
18. J. R. Gorver and B. E. Chidley, British Report AERE-R-3178, Atomic Energy Research Establishment, Harwell, England, 1960.
19. W. Bocola, A. Donato, and G. Sgalambro, *Symp. on the Management of Radioactive Wastes from Fuel Reprocessing*, IAEA, Paris, 1972, p. 449.
20. J. L. McElroy, K. J. Schneider, J. N. Hartley, J. E. Mendel, G. L. Richardson, R. W. McKee, and A. G. Blasewitz, "Waste Solidification Program Summary Report," Vol 11, *Evaluation of WSEP High Level Waste Solidification Processes*, BNWL-1667, July 1972.
21. J. A. Kelley, E. I. duPont de Nemours and Co., Savannah River Laboratory, Aiken, SC, DP-1382, May 1975.
22. J. E. Mendel, PNL 3946, Battelle Pacific Northwest Laboratories, December 1978.
23. M. J. Plodinec, G. C. Wicks, and N. E. Bibler, *The Technology of High-Level Nuclear Waste Disposal*, Vol 2, ed. P. L. Hofmann, DOE, 1982, p. 336.
24. C. M. Jantzen, M. J. Plodinec, and J. Non-Cryst, *Solids*, Vol 67, 1984, p. 207.
25. C. M. Jantzen and J. Non-Cryst, *Solids*, Vol 84 (1986), p. 215.
26. E. M. Levin, *Phase Diagrams: Materials Science and Technology*, Vol 6-III, ed. A. M. Alper, Academic Press, New York, 1970, p. 143.
27. P. B. Queneau, D. E. Gregar and L. D. May, "Application of Slag Technology to Recycling of Solid Wastes," *AIME-SME Annual Meeting, Denver, CO, February 25-28, 1991*.
28. J. M. Welch, R. P. Schuman, and J. E. Flinn, *Immobilization of Transuranic Sludge in Glass-Ceramic Materials*, EGG-FM-5709, March 1982.
29. G. J. McCarthy, *J. Mat., Sci.* Vol 8, 1973, p. 1358.
30. G. J. McCarthy and M. T. Davidson, *Am. Ceram. Soc. Bull.*, Vol 54, 1975, p. 782.
31. R. O. Schoebel, *Am. Ceram. Soc. Bull.*, Vol 54, 1975, p. 495.
32. A. E. Ringwood, V. M. Oversby and S. E. Kesson, *Proc. Seminar on Chemistry and Process Engineering for High-Level Liquid Waste Solidification*, eds. R. Odoj and E. Merz, July Conf. 42, Vol 1, 1981, p. 495.
33. P. E. D. Morgan, D. R. Clarke, C. M. Jantzen, and A. B. Harker, *J. Am Ceram. Soc.*, Vol 64, 1981, p. 249.

34. J. B. Dunson, Jr., A. M. Eisenberg, R. L. Schuyler III, H. G. Haight, Jr., V. E. Mello, T. H. Gould, Jr., J. L. Butler, and J. B. Pickett, DP-1625, E. I. duPont de Nemours & Co., Savannah River Laboratory, Aiken, SC, March 1982.
35. A. K. De, B. Luckscheiter, W. Lutze, G. Malow, and E. Schiewer, *Am. Ceram. Soc. Bull.*, Vol 55, 1976, p. 500.
36. W. Lutze, J. Borchardt, and A. K. De, *Scientific Basis for Nuclear Waste Management*, ed. G. J. McCarthy, Plenum, New York, 1979, p. 69.
37. D. R. Clarke, *J. Am. Ceram. Soc.*, Vol 64, 1981, C89.
38. A. B. Harker, D. R. Clarke, C. M. Jantzen, and P. E. D. Morgan, *Surfaces and Interfaces in Ceramic and Ceramic-Metal Systems*, eds. J. A. Pask and A. Evans, Plenum, New York, 1981, p. 207.
39. C. M. Jantzen, D. R. Clarke, P. E. D. Morgan and A. B. Harker, *J. Am. Ceram. Soc.*, Vol 65, 1982, p. 292.
40. L. P. Hatch, *Am. Scientist*, Vol 41, 1953, p. 410.
41. B. C. Slaes and L. A. Boatner, *Mat. Lett.*, Vol 2, No. 4B, 1984, p. 669.
42. B. C. Slaes and L. A. Boatner, ORNL-6168, May 1985, Oak Ridge National Lab., Oak Ridge, TN.
43. B. C. Slaes and L. A. Boatner, *L. Non-Cryst. Solids*, Vol 71, 1985, p. 103.
44. C. M. Jantzen, *Am. Ceram. Soc. Abstr.*, 1986, p. 510.
45. L. Kahl and W. Bernotat, *Am. Ceram. Soc. Abstr.*, 1986, p. 510.
46. E. R. Vance, D. J. Cassidy, K. L. Smith, and J. L. Woolfrey, *Ceramic Transactions Vol 9, Nuclear Waste Management III*, ed. G.B. Mellinger, 1990, p. 71.
47. H. W. Chan and D. G. Howitt, *Ceramic Transactions, Vol 9, Nuclear Waste Management III*, ed. G. B. Mellinger, 1990, p. 23.
48. R. C. Ewing and W. Lutze, *Ceramic Transactions, Vol 9, Nuclear Waste Management III*, ed. G. B. Mellinger, 1990, p. 33.
49. J. R. Bartlett, J. L. Woolfrey and W. J. Buykx, *Ceramic Transactions Vol 9, Nuclear Waste Management III*, ed. G. B. Mellinger, 1990, p. 45.
50. J. M. Welch, R. P. Schuman, S. P. Henslee, and R. L. Tallman, *Iron-Enriched Basalt as a Waste Form for High Level Nuclear Wastes*, EGG-FM-5758, December 1982.
51. S. O. Bates, *In Situ Vitrification Waste Form Product Evaluation Strategy*, EGG-WTD-9148, August 1990, p. 15.

52. USEPA, *Toxicity Characteristic Leaching Procedure (TCLP)*, 40 CFR 268, App. I, U.S. Federal Register, Washington, DC, 1988, p. 728.
53. M. J. Plodinec, C. M. Jantzen, and G. G. Wicks, *Scientific Basis for Nuclear Waste Management*, Vol 7, G. L. McVay ed., North-Holland, NY, 1984, p. 755.
54. M. J. Plodinec, C. M. Jantzen, and G. G. Wicks, "Advs. in Ceramics," Vol 8, *Nuclear Waste Management*, ed. G. G. Wicks and W. A. Ross, 1984, p. 491.
55. C. M. Jantzen and M. J. Plodinec, J. Non-Cryst., *Solids*, Vol 67, 1984, p. 207.
56. C. M. Jantzen, "Advs. in Ceramics," Vol 20, *Nuclear Waste Management II*, eds. D. E. Clark, W. B. White, and A. J. Machiels, 1986, p. 703.
57. S. T. Kujawa, *DOE/EPA SITE Demonstration: DOE Test Plan*, INEL/MSE report 2DOE-PAFE-D002R1, MSE, Inc., Butte, Montana, April 1991.
58. G. A. Reimann and J. M. Welch, *Electromelt Furnace Evaluation*, EGG-FM-5566, September 1981.
59. B. C. Anderson, (Westinghouse Electric, WIPP), "Overview of Waste Regulations Defining NDE/NDA Requirements," *Transuranic and Hazardous Waste Characterization Information Exchange*, Pocatello, Idaho, July 1991.
60. *Transuranic and Hazardous Waste Characterization Information Exchange*, Pocatello, Idaho, July 1991.
61. J. M. Welch, R. L. Miller, and J. E. Flinn, *Fuel and Core Storage and Disposal Development: FY-82 Immobilization of Three-Mile Island Core Debris*, EGG-FM-6059, October 1982.

Appendix A

Source Data for Waste Streams and Scenarios

Appendix A

Source Data for Waste Streams and Scenarios

A.1 Waste Stream Inventory Tables

The specific buried waste inventory data which was used as background for this report is included as follows. Table A-1 indicates the opening and closing dates for waste locations in the Subsurface Disposal Area (SDA).¹ Table A-2 indicates the evacuated container, soil, overburden, underburden and subsidence volume for the trenches and pits of interest.^{2,a} Table A-3 indicates the estimated mass of U, Pu, and Am shipped from Rocky Flats Plant (RFP) in 1954 through 1970 (see Reference 1). Table A-4 and A-5 give the number and type of containers in each trench and pit, respectively (see Reference 2 and footnote a). Table A-6 gives special considerations for waste buried in pits of interest.³ Table A-7 indicates the volumes of certain liquid wastes shipped from RFP (see footnote a).⁴ Table A-8 gives the range of metal wastes in selected trenches and pits (see footnote a).⁵ Table A-9 is a summary of the drum wastes shipped from RFP Aqueous Waste Treatment Facility by type and year (see Reference 1). Table A-10 indicates the weight and volume fractions of wastes buried at the SDA.⁶ Table A-11 gives a detailed listing of materials known to be buried in Pit 9 and indicates some mass and/or volume data.^b Additional detailed information on the contents and the location within the trenches and pits, that will be useful during actual remediation, is being generated by Waste Technology Development Department (WTDD) personnel of EG&G Idaho, Inc.

A.2 SDS Incineration & Melting Systems

The system scenarios for treatment pivot around the recommendations of the System Design Study (SDS).⁷ The two treatment systems proposed in the SDS that fall within the work scope of the JHM/PHM applications are Incineration & Melting with Low-Level Waste (LLW) Presort (2-EG-1) and Incineration & Melting with LLW Postsort (2-EG-4). In the LLW presort option an on-line assay is made to separate transuranic waste (TRUW) and LLW wastes prior to other sorting procedures common to both systems. Figure A-1 gives the process flow diagram for the system with LLW presort (see Reference 7).

The Postsort option is shown in Figure A-2. In the Postsort option, the On-Line Assay between TRUW and LLW and, hence, the LLW Processing Subsystem are eliminated. With this system, the

a. D. A. Arrenholz and J. L. Knight, "A Brief Analysis and Description of Transuranic Waste Disposal in the Subsurface Area of the Radioactive Waste Management Complex at the INEL," WTD-90-016, November 1990.

b. D. A. Arrenholz and J. L. Knight, "Historical Report of Transuranic Waste Pits and Trenches at the Subsurface Disposal Area of the Radioactive Waste Management Complex at the INEL," WTD-91-027, August 1991.

disposal options are the same, but the assay and separation of TRUW and LLW occur after the decontamination of metals, incineration of combustibles, and melting and dissolution.

The common sorting procedures occur at different stages and essentially separate into three classes: (a) TRUW for packaging and storage in a TRUW repository, (b) LLW wastes for separate treatment (from TRUW) and subsequent land disposal restriction (LDR) storage, and (c) clean off-gas, water or soils for unrestricted disposal. Additional details are discussed elsewhere (see Section 5.2 and Reference 7).

The Retrieval Subsystem (S-BE-4) is shown in Figures A-3 and A-4. It separates the soils from the non-soil containers, machinery, etc. Oversized, overly radioactive, and other waste stream materials that would be difficult to handle directly in the system are separated for special case processing requirements.

The Soils Processing Subsystem (S-EB-2) is shown in Figures A-5 and A-6. It separates the soil into TRU-contaminated soil, LL-contaminated soil, clean soil, and clean water.

The LLW Processing Subsystem (S-IT-3), is shown in Figures A-7 and A-8. It incinerates and solidifies LDR materials, separates and decontaminates metals, and separates and decontaminates/encapsulates lead. Proposed outputs include packaged TRUW for a repository, packaged LLW for LDR, clean lead, and clean stack gas.

The Metal Decontamination Subsystem (S-EG-1) is shown in Figures A-9 and A-10 sorts into TRUW metals, LLW metals, liquid/residue, and clean water. Figure A-10 also shows the general arrangement for the waste receiving, processing and packaging facility.

Table A-1. Opening and closing dates for waste locations in the SDA.

Trench	Opened	Closed	Trench	Opened	Closed	Pit	Opened	Closed
1	7-8-52	10-1-54	30	3-2-63	9-12-63	1	11-1-57	10-1-59
2	10-1-54	12-21-54	31	3-25-63	11-22-63	2	10-1-59	7-1-63
3	12-22-54	4-22-55	32	4-1-63	11-18-63	3	12-15-61	1-3-63
4	4-22-55	11-21-55	33	10-11-63	8-11-64	4	1-3-63	4-26-67
5	11-4-55	3-29-56	34	3-18-64	8-27-64	5	6-18-63	12-22-66
6	3-22-56	9-4-56	35	8-28-64	1-19-65	6	5-18-67	10-22-68
7	8-14-56	12-20-56	36	12-1-64	7-24-65	7	9-19-66	10-5-66
8	12-13-56	5-7-57	37	12-24-64	7-1-65	8	3-6-67	11-69
9	1-7-57	9-6-57	38	5-15-65	9-16-65	9	11-8-67	6-9-69
10	7-19-57	2-7-58	39	7-20-65	11-5-65	10	8-7-68	7-8-71
11	2-11-58	7-25-58	40	10-7-65	1-13-66	11	4-14-70	9-12-72
12	1-3-58	1-16-59	41	1-4-66	10-4-66	12	7-2-70	9-12-72
13	1-9-58	4-24-59	42	5-9-66	1-17-67	13	7-20-71	7-29-74
14	4-16-59	7-30-59	43	10-20-66	6-1-67	14	7-1-74	3-31-76
15	7-31-59	10-16-59	44	1-13-67	3-24-67	15	6-25-75	7-3-84
16	10-17-59	4-12-60	45	2-28-67	9-27-67	16	5-22-78	10-25-84
17	11-1-59	7-1-60	46	9-25-67	3-14-68	17	5-5-84	
18	5-10-60	7-20-60	47	2-28-68	8-5-68	18	9-1-88	
19	7-5-60	11-29-60	48	8-8-68	5-2-69			
20	12-1-60	6-30-61	49	11-18-68	6-30-69			
21	12-13-60	1-10-61	50	7-1-69	11-1-69			
22	2-1-61	4-25-61	51	10-30-69	4-8-70			
23	6-20-61	9-15-61	52	3-4-70	7-4-70			
24	10-1-61	7-31-62	53	7-1-70	10-12-70			
25	8-1-61	7-27-62	54	9-23-70	5-4-71			
26	4-13-62	8-17-62	55	4-7-71	3-12-82			
27	8-20-62	1-4-63	56	12-29-71	2-1-73			
28	12-26-62	3-12-63	57	12-28-72	6-11-74			
29	11-19-62	3-20-63	58	2-20-74	8-17-81			
			Pad	Opened	Closed			
			A	9-26-72	11-17-78			

Table A-2. Volume data for Rocky Flats TRU pits and trenches.

Location	Excavated Volume ft3	Waste Container Volume ft3	Soil Volume ft3	Overburden Volume ft3	Subsidence Volume ft3	Underburden Volume ft3
T 1	81243	16897	64346	30563	0	NA
T 2	86932	6801	80131	26544	0	NA
T 3	90658	12375	78284	26664	689	NA
T 4	93828	17788	76040	26808	750	NA
T 5	112362	17905	94457	29245	0	NA
T 6	91982	15475	76507	26856	1800	NA
T 7	87278	10729	76549	29093	0	NA
T 8	97752	14143	83610	26880	156	NA
T 9	83633	13237	70396	28891	0	NA
T 10	91474	9107	82368	26904	923	NA
P 1	379135	81819	297316	107884	0	169532
P 2	1020359	418357	602902	425975	455	544852
P 3	368394	102059	266335	236150	0	70845
P 4	955309	388494	566815	787343	0	367427
P 5	796729	286612	510117	368236	18	100428
P 6	447515	223898	223617	409313	0	191013
P 9	342416	150690	191726	256812	353	149807
P 10	1052941	538865	514076	784084	0	526471
TOTAL	6279940	2325251	3954692	3654245	5144	2120375

a. Total volume of pits and trenches = 6,279,940 ft³
Total volume of waste contained = 2,325,251 ft³
Total volume of contaminated soil = 9,734,456 ft³
Total volume of contaminated
wastes and soils = 12,059,707 ft³

Does not include wastes retrieved during early and interim waste retrieval projects.

Table A-3. Estimated quantities of uranium, plutonium, and americium in Rocky Flats wastes at the RWMC SDA.

Calendar (a) Year	U-238 (kg)	U-235 (g)	Pu-238 (g)	Pu-239 (g)	Pu-240 (g)	Pu-241 (g)	Pu-242 (g)	Am-241 (g)
1954	733	180	0.02	239	14	--	--	14
1955	979	870	0.15	1,529	95	5	0.3	26
1956	1,174	1,108	0.22	2,266	141	8	0.4	28
1957	2,147	1,616	0.30	3,184	198	12	0.5	43
1958	4,209	5,009	0.41	4,320	269	16	0.7	61
1959	3,753	11,319	0.46	4,800	299	18	0.8	62
1960	4,123	16,481	0.34	3,553	222	17	0.6	46
1961	4,311	13,921	0.53	5,538	346	26	1.0	70
1962	4,674	4,493	0.50	5,171	323	24	0.9	180
1963	1,672	6,269	1.53	15,944	996	76	2.7	204
1964	1,339	7,886	1.79	18,586	1,161	89	3.2	238
1965	4,269	4,066	2.43	25,340	1,583	122	4.3	414
1966	53,452	1,688	8.73	90,820	5,674	438	15.5	2,815
1967	53,176	1,889	5.40	56,231	3,513	271	9.6	2,129
1968	33,373	1,210	4.18	43,543	2,720	210	7.4	1,778
1969	22,721	36,259	3.25	38,046	2,376	149	6.5	4,875
1970	<u>7,084</u>	<u>14,196</u>	<u>2.58</u>	<u>24,178</u>	<u>1,517</u>	<u>105</u>	<u>5.2</u>	<u>1,834</u>
TOTALS	203,194	128,467	32.82	343,288	21,447	1,586	59.6	14,817

(a) During calendar year 1967, there were 56 grams of U-233.

Table A-4. Waste container types, numbers, and total volumes for selected trenches at the SDA.

<u>Trench No. ^a</u>	<u>Container Type</u>	<u>No. of Containers</u>	<u>Volume of Containers (ft³)</u>
1	Drums	3,376	16,747
	Other	1	150
		<u>3,377</u>	<u>16,897</u>
2	Drums	1,045	6,761
	Wooden Boxes	4	40
		<u>1,049</u>	<u>6,801</u>
3	Drums	1,242	8,655
	Wooden Boxes	6	162
	Cardboard Boxes	1,423	7,115
		<u>2,671</u>	<u>15,932</u>
4	Drums	2,416	17,761
	Wooden Boxes	1	27
		<u>2,417</u>	<u>17,788</u>
5	Drums	2,541	18,176
		<u>2,541</u>	<u>18,176</u>
6	Drums	2,283	15,462
	Wooden boxes	1	13
		<u>2,284</u>	<u>15,475</u>
7	Drums	1,497	10,729
		<u>1,497</u>	<u>10,729</u>
8	Drums	1,654	12,160
	Cardboard boxes	793	3,965
		<u>2,447</u>	<u>16,125</u>
9	Drums	1,769	13,008
	Wooden boxes	1	224
	Cardboard box	2	10
		<u>1,772</u>	<u>13,242</u>
10	Steel drums	1,236	9,089
	Cardboard boxes	7	35
		<u>1,243</u>	<u>9,124</u>

- a. The stored waste in Trenches 1-10 consisted mainly of cardboard boxes from the INEL on-site generators. Intermixed with the on-site boxes were steel drums, wooden boxes, plastic bags, and loose waste. Some Rocky Flats waste is also intermixed. Values reflect the retrieved waste removed.

Table A-5. Waste container types, numbers and total volumes for selected pits at the SDA.

<u>Pit No.</u>	<u>Container Type</u>	<u>No. of Containers</u>	<u>Volume of Containers(ft³)</u>
1	Drums	8,285	60,917
	Wooden Boxes	152	8,001
	Cardboard Boxes	2,173	12,869
	Other	2	32
		<u>10,612</u>	<u>81,819</u>
2	Drums	34,480	252,077
	Wooden Boxes	1,048	75,728
	Cardboard Boxes	3,547	17,960
	Others	443	72,592
		<u>39,518</u>	<u>418,357</u>
3	Drums	6,684	48,961
	Wooden Boxes	201	10,565
	Cardboard Boxes	3,309	30,774
	Other	62	11,759
		<u>10,256</u>	<u>102,059</u>
4	Drums	31,467	231,330
	Wooden Boxes	624	68,060
	Cardboard Boxes	2,020	16,617
	Other	268	72,487
		<u>34,379</u>	<u>388,494</u>
5	Drums	19,652	144,355
	Wooden Boxes	919	110,831
	Cardboard Boxes	970	7,773
	Other	102	23,653
		<u>21,643</u>	<u>286,612</u>
6	Drums	13,912	102,272
	Wooden Boxes	590	73,918
	Cardboard Boxes	3,523	41,242
	Other	36	6,466
		<u>18,061</u>	<u>223,898</u>
9	Drums	3,937	28,942
	Wooden Boxes	520	72,735
	Cardboard Boxes	1,932	29,571
	Other	72	19,442
		<u>6,461</u>	<u>150,690</u>
10	Drums	27,101	189,857
	Wooden Boxes	2,311	274,048
	Cardboard Boxes	914	11,830
	Other	295	63,130
		<u>30,621</u>	<u>538,865</u>

Table A-6. Special waste considerations buried in pits at the SDA.

Pit No.	Comments
1	Pit reopened in October, 1961, for disposal of some waste from the SL-1 reactor incident. Waste contained approximately 120 Curies of MFP. Highest radiation reading recorded was 10 R/h at contact. This waste is probably limited to the western end of the pit.
2	Large amounts of beta-gamma contaminated waste disposed with the TRU drums and boxes. This waste includes reactor shielding (36,000 lb), an aluminum heat exchanger (20,000 lb), drums with various contents, large (150 ft ³) concrete blocks contaminated with MFP, and other items. Also this pit contains contaminated material from the cleanup of the SL-1 incident. This pit was flooded in 1962, prior to closure.
3	NonTRU boxes from various on-site sources buried in this pit. These boxes apparently contain MFP. Six boxes (12,000 to 14,000 lb each) of intermediate-level waste (55-gal drum centered in a box, and the box was then filled with concrete shielding) buried at unknown locations in pit. SL-1 incident cleanup waste also buried in this pit.
4	MFP wastes intermixed with TRU wastes; locations are not clearly recorded (probably randomly dumped into the pit). Non-TRU waste (containers, scrap lumber, concrete, miscellaneous equipment, scrap metal, valves, and piping) generally confined to the westernmost 91 m of the pit.
5	Burial location for some of the wastes may be in error. A good possibility exists that some of the wastes may actually be outside of recorded pit boundaries.
6	Drums and boxes were not segregated during burial. A large number of boxes containing contaminated empty drums are buried in this pit.
9	Drums and boxes were not segregated. A large number of boxes containing contaminated empty drums are buried in pit.
10	Contains large number of boxes of contaminated empty drums, but the number of drums per box is not known. This pit was flooded in the spring of 1969, before it was closed.

Table A-7. Volumes of organic wastes shipped from RFP to INEL.

Year	RWMC Status	Number of Drums	(Volumes in Gallons)		
			Texaco Regal Oil	Carbon Tetrachloride	Other Organic ^a
1966	Buried	267	2,000 ^b	800 ^b	No Record
1967	Buried	5,518	22,247	14,832	4,255
1968	Buried	2,391	10,771	7,181	18,313
1969	Buried	533	4,000 ^b	1,600 ^b	2,400 ^b
Total	Buried	8,709	39,018	24,413	24,968
1970	Stored	1,092	2,528	1,685	35,135
1971	Stored	825	8,911	5,940	16,564
1972	Stored	953	11,322	7,548	10,771
1973	Stored	596	8,794	5,862	6,846
1974	Stored	572	9,158	6,106	5,356
1975	Stored	539	6,456	4,304	5,371
1976	Stored	361	4,548	3,032	4,179
1977	Stored	334	3,796	2,531	4,743
1978	Stored	471	3,388	2,259	12,431
1979	Stored	384	4,396	2,930	6,398
1980	Stored	422	5,095	3,396	7,925
1981	Stored	674	8,557	5,705	10,127
1982	Stored	480	6,736	4,491	7,670
1983	Stored	387	10,189	6,792	9,240
1984	Stored	276	8,646	5,764	120
1985	Stored	300	8,852	5,902	----- ^c
1986	Stored	463	8,617	5,744	----- ^c
1987 ^d	Stored	155	4,853	3,235	----- ^c
Total	Stored	9,284	124,842	83,226	142,876

a. Mostly 1,1,1-trichloroethane, trichloroethylene, perchloroethylene, and used oil.

b. Data estimated.

c. In 1984, this category of organic wastes were processed separately and shipped to the Nevada Test Site as low-level wastes.

d. January to June 1987.

Table A-8. Estimates of metal content in selected pits and trenches at the SDA.

Waste Location	Total Weight of Waste (kg)	Maximum Metal Weight ^a (kg)	Minimum Metal ^a Weight (kg)
Pit 1	337,300	269,840	16,865
Pit 2	7,264,000	5,811,200	363,200
Pit 3	823,500	658,800	41,175
Pit 4	5,539,000	4,431,200	276,950
Pit 5	2,968,000	2,374,400	148,400
Pit 6	2,672,000	2,137,600	133,600
Pit 9	1,357,707	1,086,166	67,885
Pit 10	6,148,000	4,918,400	307,400
Trench 1	274,500	219,600	13,725
Trench 2	123,700	98,960	6,185
Trench 3	196,500	157,200	9,825
Trench 4	267,600	214,080	13,380
Trench 5	347,200	277,760	17,360
Trench 6	305,000	244,000	15,250
Trench 7	198,800	159,040	9,940
Trench 8	208,000	166,400	10,400
Trench 9	179,300	143,440	8,965
Trench 10	110,500	88,400	5,525
TOTAL	27,962,900	22,370,320	1,398,145

a. Maximum metal weight was assumed to be 80% (worst-case scenario) of the total weight of the waste. Minimum metal weight was assumed to be 5% of the total weight of the waste.

Table A-9. Summary of drum wastes from the aqueous waste treatment facility (74 series wastes).

Year	741	742	743	744	745	746	Yearly Total
1953-1954	79 ^a	391	--	--	--	--	470
1955	155 55-gal drums 9 42-gal drums <u>164</u>	807 55-gal drums 35 42-gal drums <u>842</u>	--	Series 74R ^b : 352 55-gal drums 11 42-gal drums <u>363</u>	--	--	1,369
1956	195 55-gal drums 10 42-gal drums <u>207</u>	1,087	--	Series 74R: 356	--	--	1,650
1957	407	901	--	--	--	--	1,308
1958	369	610	--	--	--	--	979
1959	323	899	--	--	--	--	1,222
1960	556	838	--	--	--	--	1,394
1961	537	810	--	--	--	--	1,347
1962	474	993	--	--	--	--	1,467
1963	563	652	--	--	--	--	1,215
1964	552 Sludge drums 22 Cemented liquid drums ^c <u>574</u>	708 Sludge drums 1 Trash drum <u>709</u>	--	--	--	--	1,308
1965	592 Sludge drums 127 Cemented liquids <u>719</u>	799 Sludge drums 61 Cemented liquids 105 Trash drums <u>965</u>	--	--	--	--	1,802
1966	1,129 Sludge drums 174 Cemented liquids 9 Trash drums <u>1,312</u>	1,155 Sludge drums 136 Cemented liquids 276 Trash drums <u>1,567</u>	267	--	--	--	3,146
1967	1,092 Sludge drums <u>1,092</u>	1,209 Sludge drums 147 Trash drums <u>1,406</u>	5,518	375 Cemented liquid drums 148 Empty bottles in drums <u>523</u>	1,214	1,948 Empty oil drums <u>1,948</u>	11,701

Table A-9. (continued)

Year	741	742	743	744	745	746	Yearly Total
1968	802 55-gal drums 643 30-gal drums <u>1,445 (sludge only)</u>	1,521 Sludge drums 118 Trash drums <u>1,639</u>	2,391	371 Cemented liquid drums 102 Empty bottles in drums <u>473</u>	2,802	3,994 Empty oil drums 2 Heavy oils/w calcium silicate <u>3,996</u>	12,746
1969	559 55-gal drums 615 30-gal drums <u>1,174 (sludge only)</u>	1,512 Sludge drums 18 Trash drums <u>1,530</u>	533	335 Cemented liquid drums 107 Empty bottles in drums <u>442</u>	1,962	46 Trash drums, empty oil drums, broken concrete in drums <u>46</u>	5,667
1970	443 Sludge drums <u>443</u>	837 Sludge drums 4 Trash drums <u>841</u>	969	188 Cemented liquid drums 88 Empty bottles in drums <u>276</u>	2,818	27 Trash drums 9 Empty oil drums <u>36</u>	5,383
Total drums/ series	8,329 55-gal sludge drums 19 42-gal sludge drums 1,258 30-gal sludge drums 323 Cemented liquid drums <u>152</u> Trash drums <u>10,581</u>	15,729 55-gal sludge drums 35 42-gal sludge drums 719 Trash drums 197 Cemented liquid drums <u>16,680</u>	9,678	1,977 Cemented liquid drums 11 42-gal drums w/cemented liquids 445 Empty bottles in drums <u>2,433</u>	8,796	5,951 Empty oil drums 2 Drums with heavy oil w calcium silicate 73 Trash drums, concrete in drums, empty oil drums <u>---</u>	--
						GRAND TOTAL	54,194

a. All numbers represent 55-gal drums unless otherwise stated.

b. 1955-1956: Series 74R waste was effluent from the 741 and 742 treatment process. The effluent was 6N HNO₃ and was neutralized with NaOH and mixed with Portland cement in waste drums. After 1956, the effluent was pumped to the solar evaporation ponds for impoundment.

c. Cemented liquids were later identified as 744-series waste. Prior to 1964, no information is available concerning the number of cemented liquid drums included with 741- and 742-series waste drums.

d. Trash drums contain waste produced by Building 774 (AWIF) operations. The wastes primarily consist of combustible materials.

Table A-10. Weight and volume fractions of wastes stored at the RWMC.

Category	Codes	Weight Fraction ^a	Volume Fraction ^a	Density (lb/ft ³)
Combustibles	40	0.201	0.42	17.73
Sludge	36	0.327	0.18	67.22
Unknown/unclassifiable	21	0.097	0.15	24.87
Metals	15	0.222	0.086	95.87
Mixed waste	22	0.0389	0.073	19.86
Concrete, brick, particulates	38	0.0791	0.045	65.70
Nonmetals and glass	18	0.0284	0.041	25.95
Low level	7	0.00389	0.005	31.81
Remote handled	2	0.000961	0.001	25.31
NonTRU	1	0.00133	0.001	47.87
Salts	11	0.000691	0.0007	39.37

a. Weight and volume fractions of the buried TRU wastes are assumed to be same as that given for the stored TRU wastes.

Table A-11. Rocky Flats TRU pits and trenches waste disposal information.

Location	Date Opened	Ref	Date Closed	Ref	Container Type	Ref	Conditions	Ref	Waste Source (amount)	Ref	Waste Category	Ref	Specific Wastes	Ref	Waste Amounts	Ref
p-9	11-8-67	a	6-9-69	a	Drums (3921) Boxes (2029)	b	Random	b	Rocky Flats NRTS	b	Metals	b	Beryllium	f	41 gal (est)	f
													Lithium	f	238 gal (est)	f
													Sodium (and compounds)	f	3,469 gal (est)	f
													Mercury	f		
													Carbon steel	g	326,501.8 kg (est)	g
													Stainless steel	g	309,693.8 kg (est)	g
													Aluminum	g	2,337.4 kg (est)	g
													Iron	g	2,668.8 kg (est)	g
													Lead	g	7,033.3 kg (est)	g
													Zirconium	g	17,420.0 kg (est)	g
Radionuclides																
TRU																
Plutonium-238																
Plutonium-239																
Plutonium-240																
Plutonium-241																
Plutonium-242																
Americium-241																
LLW																
Uranium-234																
Uranium-235																
Uranium-238																
Cobalt-60																
MAP																
MFP																
Unidentified beta/gamma																
Inorganics																
Sodium nitrate																
Potassium nitrate																
Calcium silicate																
Portland cement																
Asbestos																
Thallium oxide																
Caustic compounds																
Sodium hydroxide																
Acids																
Hydrofluoric acid																
Hydrochloric acid																
Hydrated oxides																
Hydrated iron oxides																
Hydrated magnesium oxides																
Hydrated aluminum oxides																
20,099 gal (est)																
10,050 gal (est)																
58,775 gal (est)																
4,182 gal (est)																
87,466.8 kg (est)																
3 gal (est)																
859 gal (est)																
1,255 gal (est)																
16,075 gal (est)																

A-16

Table A-11. (continued)

<u>Date</u>	<u>Date</u>	<u>Ref.</u>	<u>Container</u>	<u>Ref.</u>	<u>Conditions</u>	<u>Ref.</u>	<u>Waste Source</u>	<u>Ref.</u>	<u>Waste Category</u>	<u>Ref.</u>	<u>Specific Wastes</u>	<u>Ref.</u>	<u>Waste Amounts</u>	<u>Ref.</u>
<u>Opened</u>	<u>Closed</u>		<u>Type</u>			(amount)								
P-9 (cont'd)										d	Hydrated silicon oxides	d		
										d	Hydrated plutonium oxides	d		
										d	Hydrated americium oxides	d		
									Organics	d	i.i.l.-trichloroethane	d	753 gal (est)	
										d	Trichloroethylene	d	565 gal (est)	
										d	Perchloroethylene	d	565 gal (est)	
										d	Carbon tetrachloride	d	3,677 gal (est)	
										d	Texaco Regal oil	d	5,875 gal (est)	
										d	Polychlorinated biphenyls	d	0.10 gal (est)	
										d	Organophosphates	d	trace amounts	
										d	Nitrobenzene	d	trace amounts	
										d	Alcohols	d	1,287 gal (est)	
										d	VERSENE (EDTA)	d	1,287 gal (est)	
										i	Ether	i	838 gal (est)	
										i	Organic acids	i	1,287 gal (est)	
										i	Gasoline	i	163 gal (est)	
										i	Ethylene glycol	i	1,287 gal (est)	
										i	Miscellaneous:	i	49 gal (est)	
										i	Used oils	i	2,378 gal (est)	
										d	Hydraulic oil	d		
										d	Gearbox oil	d		
										d	Spindle oil	d		
										d	Freon	d		
										d	Varso	d		
				b			Rocky Flats		Atypical	b	RFP fire wastes	b		
										j	6 x 6 ft stainless steel vault	j		
										d	Series 746 waste (1,302 boxes empty oil drums)	d		
									Sludges	d	Series 741	d	17,579 gal (est)	
										d	Series 742	d	23,798 gal (est)	
										d	Series 743	d	37,760 gal (est)	
										d	Series 744	d	8,043 gal (est)	
										d	Series 745	d	33,499 gal (est)	

A-17

Figure A-2. Process flow diagram for the melting and incineration with LLW postsorting system (2-EG-4).

WASTE RETRIEVAL SUBSYSTEM
(S-3E-4) - GENERAL ARRANGEMENT

JOE NO.	FIGURE	DATE
20555-005	7-7	02/22/91

Figure A-4. General arrangements for retrieval subsystem (S-BE-4).

VII-37

Figure A-5. Process flow diagram for soils processing subsystem (S-EB-4).

256'-0"

195'-0"

SOIL PROCESSING SUBSYSTEM		EO&G SYSTEM DESIGN STUDY FACILITY LAYOUT	
PROCESS: IMEL SYSTEM DESIGN STUDY SOIL PROCESSING SUBSYSTEM		EBASCO ENVIRONMENTAL	LAYOUT #10
			S-EB-2
SCALE 1"=25'		2/21/91	

Figure A-6. Facility layout for soils processing subsystem (S-EB-2).

3

Figure A-8. Facility layout flow low-level waste subsystem (S-IT-3).

Figure A-9. Unit operations for metal decontamination and sizing subsystems (S-BE-1).

Figure A-10. General arrangements for the waste receiving, processing, and packaging facility.

REFERENCES

1. M. J. Vigil, "Subsurface Disposal Area (SDA) Waste Identification," EGG-WM-8727, January 1990.
2. K. P. Guay, "Preparation of Soil Distribution in Trenches 1-10, and Pits 1-6, 9, and 10," BWP-ISV-011, in preparation.
3. D. H. Card, "History of Buried Transuranic Waste at INEL," WMP-77-3, March 1977.
4. D. E. Kudera, "Estimate of Rocky Flats Plant Organic Wastes Shipped to the RWMC," EG&G Idaho, Inc., July 24, 1987.
5. E. C. Garcia, Thurmond, S. M., and Knight, J. L., "Estimate of Metal Content of SDA," BWP-ISV-005, January 24, 1989.
6. C. R. Edinborough, "Processing Criteria for TRU Removal from RWMC Stored Waste," ERDP 2802, 1990.
7. J. L. Mayberry, W. J. Quapp, F. Feizollahi, J. C. Del Signore, and J. McFee, "Preliminary Systems Design Study Assessment Report," EGG-WTD-9594, June 1991.

Appendix B

Materials Characterization Methods

Appendix B

Materials Characterization Methods

Materials characterization of the final waste form are discussed in detail for two aspects: (1) chemical, phase, and morphological analyses and (2) chemical, mechanical, and radiation durability tests.

B.1 Chemical, Phase and Morphological Analyses

The purpose of chemical analysis is to determine the elemental composition of the final waste form as a whole, by regions, and of the phases in each region. The purpose of phase and morphological analyses is to identify the crystallographic phases of the bulk and in the regions. The molten slag is a complex elemental system which can form multiple phases while solidifying. During casting of the monolith, different regions of the cast will have different cooling rates and this will be reflected by the formation of heterogeneous phases in the monolith. Fast cooling outer regions of the monolithic bulk will vitrify to form glasses while the slow cooling inner regions will solidify into crystalline phases. Due to thermal diffusion effect, some glasses in the intermediate regions will partially devitrify to crystalline materials. The structure and elemental composition of each region will reveal if any waste components have segregated into less durable phases or migrated into interfaces between regions or the grain boundaries of crystalline phases.

The chemical, mechanical, and the irradiation tests supplemented by the material characterizations will provide the information on the overall durability of the monolithic final waste form. Any region in the monolith which shows strong departure from the statistical mean will be identified as a potential high release site.

Several analytical techniques are applicable to these types of evaluations. Each technique complements each other for complete analysis of the waste form products. Table B-1 summarizes the available materials characterization techniques for the characterization of the final waste form. These techniques will be discussed separately below.

Inductively Coupled Plasma Atomic Emission Spectroscopy - ICP

The ICP atomic emission spectroscopy can be applied to determine the overall elemental composition of different regions of the monolithic bulk material. The ICP will also provide the elemental composition to be used to determine normalized release in the durability tests.

Table B-1. Summary table for final waste form material characterization.

Techniques	Functions
ICP	Elemental analysis in the bulk, regions and in leachates.
AA	Elemental analysis in the bulk, regions and in leachates
ICP-MS	Elemental and molecular functional group analysis
SEM	Morphology, particle sizes, phase identification, phase percent, defects, density determination, grain boundary and interfacial phases analysis (high magnifications and resolutions)
EDXS/WDXS	Auxiliary analytical functions of the SEM Semi-quantitative or quantitative elemental analysis, empirical chemical compositions in phases
X-ray Maps	Auxiliary analytical functions of EDXS/WDXS Detailed elemental distributions in phases
OM	Morphology, particle sizes, phase identification, phase percent, defects, density determination, grain boundary and interfacial phases analysis (low magnifications and resolutions)
XRD	Crystalline phase identification, phase amount determination and particle size analysis
STEM	SEI mode - Scanning Electron Microscopy functions TEI mode - Transmission Electron Microscopy functions, crystalline phases identification by electron diffraction, morphology and phase analysis by bright field and dark field imaging
XPS	Elemental analysis, redox state information for the final waste form, oxidation states and the bonding environment of the bonding elements, provide information on leach surface revealing the preferential leach sites
SAM	Elemental analysis, local chemical bonding information, elemental concentration distribution by depth profiling, Auger electron maps reveal elemental distributions, provide information on leach surface revealing the preferential leach sites

ICP-Mass Spectroscopy - ICP-MS

This technique can be used to augment the elemental analyses to yield mass fragment information of the molecular functional groups on the compound. Since the final waste form is an extremely complex system, ICP-MS may not be very useful in this regard.

Atomic Absorption - AA

The atomic absorption spectroscopy can be applied to determine the overall elemental composition of different regions of the monolithic bulk material. The AA will also provide the elemental composition to be used to determine normalized release in the durability tests.

Scanning Electron Microscopy - SEM

Scanning electron microscopy makes use of either secondary electrons or back scattered electrons for image analysis. SEM can be applied to phase identification, morphology analysis, particle size analysis, phase percent determination, defect formation, density determination, grain boundary and interfacial phase analysis, etc. The scanning electron microscope is a powerful instrument for detailed material characterizations because it has much higher magnifications and resolutions than an optical microscope.

Energy or Wavelength Dispersive X-ray Spectroscopy - EDXS/WDXS

These two are augmentational analytical techniques to SEM. They provide semi-quantitative elemental analysis for the overall final waste form and for different regional composition. The approximate chemical formulation of phases can be inferred from semi-quantitative or quantitative analyses. X-ray mappings can provide detailed elemental distributions and segregations in all phases.

Optical Microscopy - OM

Optical microscopy (OM) can be used for phase identification, morphology analysis, particle size analysis, phase percent determination, defect analysis, density determination, grain boundary phase analysis, and interface segregation phenomena. The optical microscope is extremely easy to operate and is only good for quick preliminary analysis because of its low magnifications and resolutions. Specimen preparations for electron and optical microscopes are moderately labor intensive.

X-ray Diffraction Analysis - XRD

XRD can be used to identify the structure of crystalline materials and their corresponding phase amount in the sampling region, and for particle size analysis. When used in conjunction with the SEM, EDXS/WDXS, and x-ray mapping data, the specific crystalline phases that result from different cooling history in different regions of the monolith can be determined. Knowledge of the crystalline morphology will help determine how waste components are incorporated into the final waste form, allow for comparison to natural analogs, and assist in predicting its long-term behavior.

Scanning Transmission Electron Microscopy - STEM

This instrumentation combines the techniques of secondary electron imaging (SEI) and transmission electron imaging (TEI) for materials analyses. In the SEI mode it functions like a SEM. In the TEI mode it functions like a TEM and determines the crystal structure of all crystalline phases by electron diffraction. The morphology, defect structures, grain boundary phases (both crystalline and glasses), etc. can be identified by using both bright field and dark field imaging techniques. Micro-micro electron diffraction techniques can be used to identify minute phases within a minor phase. STEM has higher magnifications, higher resolutions, and wider capabilities than an SEM but the sample preparation is extremely labor intensive. The instrumentation is particularly useful when grain boundary phases and interfacial segregations are studied.

X-ray Photoelectron Spectroscopy - XPS

Formerly known as ESCA, XPS uses a high energy x-ray beam for surface characterization. XPS is useful in determining the redox state, the $\text{Fe}^{2+}/\text{Fe}^{3+}$ ratio in the final waste form. The redox state of the final waste form provides an indication to the valance state expected for the waste components and will help to predict in which phase the waste components will be partitioned in the final waste form. For example, if the condition in the slag melt is sufficiently reducing, transition elements, lead and cadmium may be partitioned to the bottom of the melter as a metal melt. XPS is also useful for complete elemental analysis with the exception of hydrogen and helium. XPS can reveal the oxidation state, the bonding environment of an ion, and the elemental compositions in a phase. Since XPS is a surface analysis tool, it analyzes the top 10 nm layer of the material, it can provide information on a leached surface revealing the preferential leach sites.

Scanning Auger Electron Microprobe - SAM

This technique uses a highly focused high energy electron beam for surface and image analysis. Similar to XPS, it will perform elemental analysis and provide local chemical bonding information of elements in compounds. In situ sputtering can provide depth profiling of elements in the material. Auger electron mappings can be applied to reveal elemental distributions or segregation in the material. Similar to XPS, it can provide information on a leached surface revealing the preferential leach sites.

B.2 Chemical Durability Tests

The following discussion on the chemical durability testing has been paraphrased from Bates¹ and can be applied to the evaluation of the final waste form by ex situ high temperature thermal processing since the final waste forms are very similar.

There are currently no specific durability specifications established for ISV/IEB final waste forms. The minimum expected testing requirements will be those currently established for landfill disposal. Since September 1990, the Environmental Protection Agency (EPA) toxicity characterization leaching procedure (TCLP)² has replaced the Extraction Procedure Toxicity Test (EPTox). Passing the test only classifies the ISV/IEB waste final form as satisfying the RCRA criteria for EPA designated toxic metals leach characteristics. However, the TCLP test procedures neither address the radioactive components, provide an assessment for the long-term durability, nor make a

comparison to other highly durable final waste forms or natural analogs. For each type of the durability tests, all major phases within the ISV/IEB final waste form should be tested, if possible. Where multiple phases cannot be separated, such as when devitrification produces an intimate mixture of different small grain crystalline phases, these multiphase mixtures should be tested as a single phase.

Sufficient replicates should be performed for each test sample to ensure the precision and accuracy of each test can be determined. The cost, amount of available samples, and the specific durability tests will be the limiting factors to the number of replicates. Since no specific release requirements (except TCLP) have been established for mixed and low-level TRU waste forms, no specific confidence limits have been set.

Regulatory Required Tests - TCLP

The required regulatory test for the retention of waste components is the TCLP tests. Waste is hazardous by definition if it displays the characteristics of ignitability, reactivity, corrosiveness, and toxicity. After being formed at temperatures $>1300^{\circ}\text{C}$, the ISV/IEB final waste forms are neither ignitable, reactive, or corrosive. The TCLP tests are designed to simulate the rainwater leaching process of certain metals that a final waste form would experience if disposed of in a sanitary landfill. The maximum allowable concentration limits for the EPA designated metals is listed in Table B-2. No organics will be present in the ISV/IEB final waste form because of the exceedingly high processing temperatures. Therefore, no organic analysis will be required. The test consists of extracting 100 g of the powdered ISV/IEB final waste form with 1600 g of deionized water. Acetic acid is used to maintain the pH of the leaching fluid at 2.88 ± 0.05 or 4.93 ± 0.05 . The procedure required the use of one of the pH values for the leaching solution and temperatures between 20°C and 40°C for a duration of 24 hours. The extract is then analyzed by ICP.

Table B-2. Maximum allowable concentrations for EPA designated metals.

Elements	Maximum Concentration (mg/liter)
Arsenic (As)	5.0
Barium (Ba)	100.0
Cadmium (Cd)	1.0
Chromium (Cr)	5.0
Lead (Pb)	5.0
Mercury (Hg)	0.2
Selenium (Se)	1.0
Silver (Ag)	5.0

MCC-1 Static Leach Test

The MCC-1 static leach test³ measures the elemental mass loss of a glass sample as a function of time. For this test, a glass monolith is suspended within a sealed teflon container. The surface

area to volume ratio (surface area of sample/volume of leachant, SA/V) is selected nominally 10 m^{-1} . The leachant can be a synthetic ground water, a synthetic brine, or reagent water. The sealed container is maintained at 90°C for 3, 7, 14, or 28 days. The test results are based on leachate elemental analysis from which the total concentrations of materials leached from the sample are determined. The most commonly used test parameters are a SA/V of 10 m^{-1} in deionized water at 90°C for 28 days. These should be used for ISV/IEB testing to allow for comparison with the large amount of data. One drawback for the MCC-1 test is that it requires a small monolithic sample. Inhomogeneities in the test samples, such as varying amounts of exposed phases, may result in inconsistent data. Therefore, MCC-1 test procedure is more suitable for one-phase materials.

MCC-3 Agitated Powder Leach Test

The MCC-3 agitated powder leach test (see Reference 3) is similar to the MCC-1 test procedure. The only differences are (a) specimens from the final waste form are grounded to powders, and (b) powder and leachant are agitated by rotating the teflon container. The elemental concentrations from MCC-3 tests are estimated to be representative of the long-term extrapolation of MCC-1 test results. This objective is achieved more rapidly in the MCC-3 test because higher SA/V ratios are used than those for the MCC-1 tests. For evaluation of ISV/IEB final waste forms, the test should be conducted with a SA/V of 2000 m^{-1} in deionized water for 28 days (a large number of 7 to 90 day data also exist). Because of the higher SA/V used in the MCC-3 testing compared to that used for MCC-1 testing, the leachants in the MCC-3 tests became saturated much sooner than the leachants in the MCC-1 tests. This saturation slows the dissolution process. Therefore, *direct* comparison of the normalized release values from the MCC-1 and MCC-3 tests is not appropriate. Since MCC-3 tests use powdered samples, combination of glass and crystalline phases may be tested together.

To allow for comparison of leach test results from final waste forms with different compositions, results are given in terms of normalized elemental mass release for the MCC-1 and MCC-3 tests and normalized concentration for the MCC-3 test. Normalized elemental mass releases can be calculated using the following equation:

$$NR_i = m_i / (F_i \times SA)$$

where

NR_i = normalized mass release of element i (g/m^2)

m_i = mass of element i in leachate (g)

F_i = fraction of element i in final waste form (dimensionless)

SA = surface area of monolith (m^2).

The following equation can be used to calculate normalized elemental concentrations:

$$NC_i = C_i / F_i$$

where

NC_i = normalized concentration of element i (g/m^3)

C_i = concentration of element i in leachate (g/m^3)

F_i = fraction of element i in final waste form (dimensionless).

Forward Rate of Dissolution (K_+)

The fastest rate at which a glass/ceramic will dissolve is the forward rate of dissolution (K_+).^{4,5,6} This parameter has the most technical relevance when evaluating the dissolution behavior of different final waste glasses. The K_+ will indicate the durability of the final waste form under the condition of dynamic flow of unsaturated leachants (ground water).

To understand the forward rate, it is beneficial to discuss the following three different regimes typically observed in glass dissolution:

1. The time in which the glass first contacts a leachant and the glass dissolution rate is inhibited by any solubility effects. In this period the leachant is highly unsaturated.
2. A transient regime where the increase in the concentrations of the dissolved components in the leachate impedes the dissolution rate through solubility effects.
3. A steady-state regime in which the dissolution rate is constant because the leachant has reached saturation i.e., reaching an equilibrium solubility product constant.

Typical release data can be plotted as elemental concentration in the leachate versus $(SA/V)^*t$ which shows three different regions (see Figure B-1). The plot is rather sensitive to SA/V and at large values of SA/V the slope of region 1 will increase much steeper than small values of SA/V .

Low values of $(SA/V)^*t$ are analogous to the ambient conditions expected for the ISV/IEB waste form as unsaturated surface water percolated past the final waste form. Because the ISV/IEB final waste form will be in a near-surface environment where water flow rates will probably be relative high, saturation of the water may not occur and the forward rate of dissolution will limit the release rate. However, the K_+ is strongly temperature dependent. Because of the high durability of the ISV/IEB waste forms, it may not be possible to conduct leach tests at ambient ground temperatures ($<20^\circ\text{C}$) and have concentrations in the leachate above analytical detection limits. Conducting leach testing at higher temperatures (40°C to 90°C) will provide adequate leachate concentrations. If conducted at three or more temperatures, the K_+ 's Arrhenius activation energy can be determined, which will allow the temperature dependence to be established and then calculate the K_+ at ambient temperatures.

B.3 Physical Durability Tests

The physical durability of the final waste form can be evaluated using a variety of mechanical test methods.

(Surface Area/Leachate Volume) * Time

Figure B-1. Release curve for leach tests.

Impact Test

This test will reveal the resistance of the monolith during impact to generate breathable fines. This test is not applicable to small final waste forms such as water granulated marbles. This test would be necessary to satisfy TRAMPAC requirements.

Bending Test

This test will reveal the fracture toughness of the final waste form. Either a three-point or a four-point bending test can be performed on the specimens to measure the fracture toughness of the material. Large sampling of the bending test on core drilled specimens from different regions of the monolith will provide a statistical average of the fracture toughness of the final waste form.

Indentation Test

This test will reveal the hardness of the final waste form. Large sampling of indentation test on core drilled specimens from different regions of the monolith will provide a statistical average of the hardness of the final waste form.

Splitting Tensile Strength Test

The splitting tensile strength test will give the maximum strength of the final waste form. This test is very sensitive to the surface condition and is a strong function of the surface microcrack density.

B.4 Radiation Durability Tests

Simulated Radiation Damage Test

This test will provide the comparative resistance of the amorphous and the crystalline phases in the final waste form to atomic displacement and ionization damage due to internal radiation source effects. To irradiate the final waste forms with high energy electron beams, gamma rays, and ion source can simulate the radiation damage tests. The internal radiation damage can produce bubbles, gas generation, atomic displacement, and ionization of the elements by high velocity radionuclides. These changes have important consequences for the durability of the final waste forms.

REFERENCES

1. S. O. Bates, EGG-WTD-9184, August 1990, p. 15.
2. USEPA, *Toxicity Characteristic Leaching Procedure (TCLP)*, 40 CFR 268, App. I, U.S. Federal Register, Washington, D.C., 1988, p. 728.
3. *Nuclear Waste Materials Handbook*, DOE/TIC-11400, Rev 7, Technical Information Center, Springfield, Virginia, 1986.
4. J. G. Carter, S. O. Bates, and G. D. Maupin, PNL-6174, Pacific Northwest Laboratory, Richland, Washington, 1987.
5. B. C. Bunker, G. W. Arnold, E. K. Beauchamp, and D. E. Day, *J. Non-Cryst. Solids*, Vol 58, 1983, p. 295.
6. N. Kawanishi, H. Igarashi, H. Nagaki, and Tsunoda, PNCT N831-80-01, Power Reactor and Nuclear Fuels Corporation, Japan, 1980.
7. H. W. Chan and D. G. Howitt, Ceramic Transactions, Vol 9, *Nuclear Waste Management III*, ed. G. B. Mellinger, 1990, p. 23.
8. R. C. Ewing and W. Lutze, Ceramic Transactions, Vol 9, *Nuclear Waste Management III*, ed. G. B. Mellinger, 1990, p. 33.

END

**DATE
FILMED
9 / 16 / 92**