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Prepared for the U.S. Department of Energy
under Contract DE-AC05-76RL01830

Secondary Waste Form Down-Selection Data Package—DuraLith

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JH Westsik, Jr.

September 2011

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Pacific Northwest National Laboratory
Richland, Washington 99352

Summary

The Hanford Site in southeast Washington State has 56 million gallons of radioactive and chemically hazardous wastes stored in 177 underground tanks (DOE 2010). The U.S. Department of Energy Office of River Protection, through its contractors, is constructing the Hanford Tank Waste Treatment and Immobilization Plant (WTP) to convert the radioactive and hazardous wastes into stable glass waste forms for disposal. Within the WTP, the pretreatment facility will receive the retrieved waste from the tank farms and separate it into two treated process streams. These waste streams will be vitrified, and the resulting waste canisters will be sent to offsite (high-level waste) and onsite (immobilized low-activity waste) repositories. As part of the pretreatment and immobilized low-activity waste processing, liquid secondary wastes will be generated that will be transferred to the Effluent Treatment Facility on the Hanford Site for further treatment. These liquid secondary wastes will be converted to stable solid waste forms that will be disposed of in the Integrated Disposal Facility.

To support the selection of a waste form for the liquid secondary wastes from the WTP, Washington River Protection Solutions has initiated secondary waste form testing work at Pacific Northwest National Laboratory. In anticipation of a down-selection process for a waste form for the Solidification Treatment Unit to be added to the Effluent Treatment Facility, Pacific Northwest National Laboratory is developing data packages to support that down-selection. The objective of the data packages is to identify, evaluate, and summarize the existing information on the four waste forms being considered for stabilizing and solidifying the liquid secondary wastes. This data package developed for the DuraLith waste form includes information available in the open literature and from data obtained from testing currently underway.

DuraLith is an alkali-activated geopolymer waste form developed by the Vitreous State Laboratory at The Catholic University of America (VSL-CUA) for encapsulating liquid radioactive waste. A DuraLith waste form developed for treating Hanford secondary waste liquids is prepared by alkali-activation of a mixture of ground blast furnace slag and metakaolin with sand used as a filler material.

Based on optimization tests, solid waste loading of ~7.5% and ~14.7% has been achieved using the Hanford secondary waste S1 and S4 simulants, respectively. The Na loading in both cases is equivalent to ~6 M. Some of the critical parameters for the DuraLith process include hydrogen generation and heat evolution during activator solution preparation using the waste simulant, heat evolution during and after mixing the activator solution with the dry ingredients, and a working window of ~20 minutes to complete the pouring of the DuraLith mixture into molds. Results of the most recent testing indicated that the working window can be extended to ~30 minutes if 75 wt% of the binder components, namely, blast furnace slag and metakaolin are replaced by Class F fly ash.[1]

A preliminary DuraLith process flow sheet developed by VSL-CUA for processing Hanford secondary waste indicated that 10 to 22 waste monoliths (each 48 ft^3 in volume) can be produced per day. There are no current pilot-scale or full-scale DuraLith plants under construction or in operation; therefore, the cost of DuraLith production is unknown.

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[1] Ian L. Pegg, VSL-CUA, Personal Communication, April 19, 2011.

The results of the non-regulatory leach tests, U.S. Environmental Protection Agency (EPA) Draft 1313 and 1316 conducted on Waste Simulant S1-optimized DuraLith specimens indicated that the concentrations of Resource Conservation and Recovery Act metals (Ag, Cd, Cr, Hg, and Pb) in the leachates were well below the Universal Treatment Standard limits in 40 CFR 268.48. The data from the EPA draft 1315 leach test showed that leachability index (LI) values for contaminants of concern (COCs), namely ^{99}Tc and I, ranged from 8.2 to 11.4 and 4.3 to 7.5, respectively. These values indicate that DuraLith meets the LI target for ^{99}Tc (>9) but does not meet the LI target (>11) for I. These targets need to be validated and verified based on more recent and future Integrated Disposal Facility performance assessments.

Results of Toxicity Characteristic Leaching Procedure (EPA Method 1311) conducted on Waste Simulant S1-optimized DuraLith specimens, indicated that the concentrations of Resource Conservation and Recovery Act metals (Ag, As, Cd, Cr, Hg, and Pb) in the leachates were well below the Universal Treatment Standard limits in 40 CFR 268.48. The data from the ANSI/ANS-16.1 leach test showed that LI values for one COC, namely Re (as a Tc surrogate), ranged from 8.06 to 10.81. The LI value for another COC, namely I, was not measured in this test.

The results of the compressive strength testing of Waste Simulant S1-optimized DuraLith specimens indicated that the monoliths were physically robust with compressive strengths ranging from 115.5 MPa (16,757 psi) to 156.2 MPA (22,667 psi).

Acknowledgments

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Acronyms and Abbreviations

ANS	American Nuclear Society
ANSI	American National Standards Institute
ART	Advanced Remediation Technologies
ASTM	American Society for Testing and Materials
BFS	blast furnace slag
CFR	Code of Federal Regulations
COC	contaminant of concern
CUA	The Catholic University of America
DE	Dose Equivalent
DIW	deionized water
DOE	U.S. Department of Energy
DST	double-shell tank
EC	electrical conductivity
Ecology	Washington State Department of Ecology
EDS	energy dispersive spectrometry
Eh	redox potential
EPA	U.S. Environmental Protection Agency
ETF	Effluent Treatment Facility
EXAFS	extended absorption fine structure
FBSR	fluidized bed steam reformer
gpm	gallons per minute
HLW	high-level waste
HSW	Hanford secondary waste
IDF	Integrated Disposal Facility
IHLW	immobilized high-level waste
ILAW	immobilized low-activity waste
LAW	low-activity waste
LDR	Land Disposal Restrictions
LERF	Liquid Effluent Retention Facility
LI	leachability index
LLC	limited liability company
LLW	low-level waste
LS	liquid to solid
MK	metakaolin
NMR	nuclear magnetic resonance
NRC	U.S. Nuclear Regulatory Commission

OPC	ordinary Portland cement
ORP	DOE Office of River Protection
PA	performance assessment
PCT	Product Consistency Test
PNNL	Pacific Northwest National Laboratory
PTE	potential to emit
PUF	Pressurized Unsaturated flow
RCRA	Resource Conservation and Recovery Act
SALDS	State-Approved Land Disposal Site
SBS	submerged-bed scrubber
SBW	sodium-bearing waste
SEM	scanning electron microscopy
SPFT	Single Pass Flow Through
SRNL	Savannah River National Laboratory
SSW	solidified secondary waste
TCLP	Toxicity Characteristic Leach Procedure
TOC	total organic carbon
TRU	transuranic
UTS	universal treatment standard
VHT	Vapor Hydration Test
VSL	Vitreous State Laboratory
WAC	Washington Administrative Code
WESP	wet-electrostatic precipitator
WRPS	Washington River Protection Solutions, LLC
WTP	Hanford Tank Waste Treatment and Immobilization Plant
XANES	X-ray absorption near edge structure
XRD	X-ray diffraction

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1.0 Introduction

The Hanford Site in southeastern Washington State has 56 million gallons of radioactive and chemically hazardous wastes stored in 177 underground tanks (Certa and Wells 2010). The U.S. Department of Energy (DOE), Office of River Protection (ORP), through its contractors, is constructing the Hanford Tank Waste Treatment and Immobilization Plant (WTP) to convert the radioactive and hazardous wastes into stable glass waste forms for disposal. Within the WTP, the pretreatment facility will receive the retrieved waste from the tank farms and separate it into two treated process streams. The pretreated high-level waste (HLW) mixture will be sent to the HLW Vitrification Facility, and the pretreated low-activity waste (LAW) stream will be sent to the LAW Vitrification Facility. The two WTP vitrification facilities will convert these process streams into glass, which will be poured directly into stainless steel canisters. The immobilized HLW (IHLW) canisters will ultimately be disposed of at an offsite federal repository. The immobilized LAW (ILAW) canisters will be disposed of onsite in the Integrated Disposal Facility (IDF). As part of the pretreatment and ILAW processing, liquid secondary wastes will be generated that will be transferred to the Effluent Treatment Facility (ETF) on the Hanford Site for further treatment. These liquid secondary wastes will be converted to stable solid waste forms that will be disposed of in the IDF. Liquid effluents from the ETF will be discharged through the State-Approved Land Disposal Site (SALDS).

The ETF is an existing operating facility on the Hanford Site. It is a Resource Conservation and Recovery Act (RCRA)-permitted, multi-waste treatment and storage facility that can accept Washington State-regulated dangerous, low-level, and mixed wastewaters for treatment. The ETF receives, treats, and disposes of liquid effluents from cleanup projects on the Hanford Site. The ETF handles treated effluent under the ETF State Wastewater Discharge Permit and solidified liquid effluents under the Washington State Department of Ecology (Ecology) Dangerous Waste Permit. The ETF lacks the capacity to treat the liquid process effluents from the WTP once it comes on line for operations.

Milestone M-047-00 of the *Hanford Federal Facility Agreement and Consent Order* (Ecology et al. 1989) requires that DOE “complete all work necessary to provide facilities for management of secondary liquid waste from the WTP” by “the date that the WTP achieves initial plant operations.” Interim milestones are to be negotiated by June 30, 2012. DOE is considering a non-major system acquisition project for a Secondary Liquid Waste Treatment Project to add the needed capacity to the ETF (DOE 2011). Among the alternatives to be evaluated for providing the needed capacity for handling the WTP liquid secondary wastes are

- Upgrade ETF, plus construct a Solidification Treatment Unit
- Upgrade ETF, with new ion exchange facilities, plus construct a Solidification Treatment Unit
- Upgrade ETF, plus recycle evaporator concentrates back to tank farms by truck or pipeline
- Provide additional evaporative capacity, plus use fluidized bed steam reforming.

Washington River Protection Solutions (WRPS), a prime contractor to DOE, is responsible for the ETF upgrades needed to receive secondary liquid wastes from the WTP at Hanford. In planning for the Secondary Liquid Waste Treatment Project, WRPS anticipates two down-selections. The first down-selection will evaluate the alternatives and options for providing the necessary capacity for treating the secondary liquid wastes from WTP and other Hanford Site liquid waste generators. Then, should the preferred alternative include adding a Solidification Treatment Unit, a second down-selection would evaluate alternative waste forms for solidifying treated wastes from the ETF.

To support the selection of a waste form for the liquid secondary wastes from WTP, WRPS has initiated secondary waste form testing work at Pacific Northwest National Laboratory (PNNL). In 2009, preliminary screening of waste forms was conducted to assess the viability of alternative waste forms for the solidification of the liquid secondary wastes (Pierce et al. 2010a; Pierce et al. 2010b). A testing program was initiated to further develop, optimize, and characterize the Cast Stone, Ceramicrete, and DuraLith waste forms to stabilize/solidify the anticipated liquid secondary wastes. Testing was also conducted on a previously prepared fluidized bed steam reformer (FBSR) waste form to develop a suite of comparable test results such that the performance of all four candidate waste forms could be evaluated.

In anticipation of a down-selection process for a waste form for the Solidification Treatment Unit, PNNL is developing data packages to support that down-selection. The objective of the data packages is to identify, evaluate, and summarize the existing information on the four waste forms being considered for stabilizing and solidifying the liquid secondary wastes. The information included will be based on information available in the open literature and from data obtained from testing currently underway.

1.1 Origin and Disposition of WTP Liquid Secondary Wastes

The WTP includes three major treatment facilities, including a pretreatment building, a HLW vitrification building, and a LAW vitrification building. Liquid wastes, sludges, and saltcake retrieved from the underground storage tanks will be piped to the pretreatment building. There, the wastes will be separated into a low-volume, HLW stream containing most of the actinides, cesium, and strontium as well as a large-volume, LAW stream with most of the sodium and aluminum. From an environmental protection perspective, the largest fractions of the technetium-99 (^{99}Tc) and iodine-129 (^{129}I) inventory in the tanks, both long-lived radionuclides, are expected to reside in the LAW stream. The HLW stream will be transferred to the HLW vitrification building where it will be combined with glass-forming chemicals and melted in a high-temperature melter. The resulting molten glass will be poured into stainless steel canisters to cool and sit in storage until it can be shipped to a federal repository. Similarly, the LAW stream will be piped to the LAW vitrification building where it will be melted with glass formers in a high-temperature melter and poured into steel canisters for disposal in IDF.

Secondary liquid wastes will be generated in the pretreatment and vitrification buildings. Figure 1.1 shows a schematic of the sources for the secondary wastes. In the pretreatment building, a front-end evaporator will be used to concentrate liquid wastes received from the underground storage tanks as well as liquid process effluents from the HLW vitrification building. A back-end evaporator will be used to concentrate the LAW from the pretreatment process plus condensates from the LAW melter primary off-gas treatment stream. Condensates from the front-end and back-end evaporators will be collected in process condensate collection tanks.

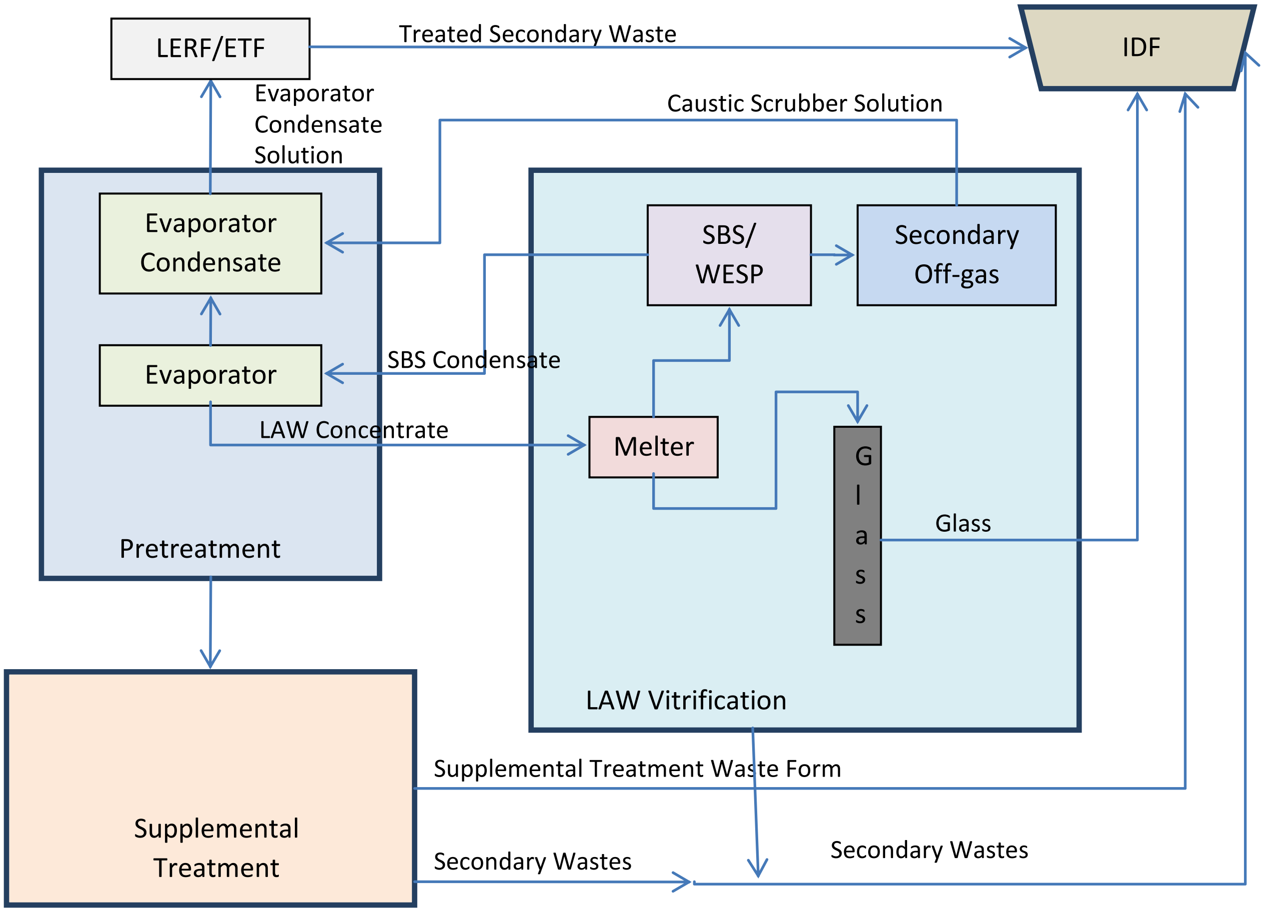

Figure 1.1. Schematic of Secondary Waste Sources

Both the HLW and the LAW vitrification facilities include off-gas treatment systems to treat the gaseous effluents from their respective glass melters. These effluents include water vapor, chemicals that are volatile at the elevated melter temperatures, and particulates. In each vitrification process, the melter off-gas passes through primary off-gas treatment systems that include submerged-bed scrubbers (SBSs) and wet-electrostatic precipitators (WESPs). Condensates from the HLW SBSs and WESPs are recycled to the pretreatment front-end evaporator. Condensates from the LAW SBSs and WESPs are recycled to the pretreatment back-end evaporator. In addition, the LAW vitrification system includes a secondary off-gas treatment system that includes a final caustic scrubber. A small fraction of the total ^{99}Tc and ^{129}I inventory to the LAW vitrification facility is expected to be captured in the caustic scrubber solution. That caustic scrubber solution is recycled back to the condensate collection tanks. Collectively, the pretreatment evaporator condensates and the LAW melter off-gas caustic scrubber solution form the secondary waste stream that is transferred from WTP to ETF for disposition.

The LAW melter off-gas SBS and WESP condensates are recycled back to the pretreatment facility and ultimately back to the LAW melter. Under some operational scenarios, some or all of the condensate from the LAW melter off-gas SBS and WESP would go directly to a secondary waste stream exiting the WTP. For example, in an "early LAW" scenario, the LAW melter would begin operations using selected tank wastes before the pretreatment facility came on line. In this case, the SBS and WESP condensates would be combined with the caustic scrubber as a single liquid secondary waste stream from the WTP. In another scenario, a fraction of the SBS/WESP condensate would be bled from the recycle stream that is sent back to the pretreatment facility to limit the buildup of constituents in the LAW melter feed that would reduce the waste loading in the LAW glass. In some recent secondary waste form testing, a 10% fraction of the SBS/WESP condensate was assumed to be bled off and combined with caustic scrubber in the secondary waste stream to ETF.

Currently defined secondary waste streams originate from the WTP and do not consider alternative supplemental treatment technologies. A second LAW melter facility would operate under the same assumptions as the first LAW melter facility. In the baseline case, approximately 626 Mgal of radioactive dangerous liquid effluent (secondary waste from the WTP, the second LAW facility, the 242-A Evaporator, an aluminum removal facility, and supplemental transuranic [TRU] treatment system) is projected to be treated by the ETF over the duration of the treatment mission (Certa and Wells 2010).

1.2 Identification of Waste Forms

Numerous waste forms have been evaluated for stabilizing and solidifying radioactive and hazardous wastes. Radioactive HLWs from nuclear fuel reprocessing are converted to a glass waste form in stainless steel canisters for disposal at a federal repository. Liquid low-level wastes (LLW) and mixed radioactive/hazardous wastes are typically stabilized and solidified before disposal in near-surface facilities. Spence and Shi (2005) provided a review of inorganic and organic binders that have been used for waste stabilization. Several recent studies have evaluated technologies specifically for solidifying WTP liquid secondary wastes. In 2006, PNNL completed an evaluation of three low-temperature waste forms, including an alkali-aluminosilicate hydroceramic cement, DuraLith alkali aluminosilicate geopolymer, and Ceramicrete phosphate-bonded ceramic (Russell et al. 2006). Alternatives to vitrification and Portland cement-based grouts were identified through an unrestricted request for proposals. Relatively mature, low-temperature (<150°C) processes with the feasibility of deployment within 1 to 2 years were favored by the evaluation criteria. That study demonstrated the potential of DuraLith alkali aluminosilicate geopolymer and Ceramicrete phosphate-bonded ceramic as adequate waste forms for the secondary wastes. As part of the Advanced Remediation Technologies (ART) program, THOR treatment technologies and Savannah River National Laboratory (SRNL) demonstrated the feasibility of an FSBR granular product encapsulated in a geopolymer matrix using an early LAW secondary waste stream composed of LAW off-gas treatment condensates that would normally be recycled within the WTP plant (TTT 2009).

The first activity for the Secondary Waste Form Testing project at PNNL was to conduct a literature survey to identify and evaluate candidate waste forms for solidifying the secondary wastes (Pierce et al. 2010a). In addition to the baseline Cast Stone Portland cement-based waste form and the DuraLith, Ceramicrete, and FBSR waste forms; several less mature technologies, including several aluminosilicates and an iron-oxide mineral called goethite with the capacity to specifically retain technetium, were identified. In parallel, WRPS issued a call for expressions of interest for secondary waste immobilization technologies. Responses to that call included a glass waste form produced with the Geomelt Vitrification Technology, a waste form based on the synroc ceramic titanate mineral, and a Nochar waste form prepared from a blend of acrylics and acrylamide copolymers (Pierce et al. 2010a).

Based on the technical literature and previous testing, four waste forms were selected for further testing and evaluation for stabilizing and solidifying WTP liquid secondary wastes:

- Cast Stone Portland-cement based waste form
- Ceramicrete phosphate bonded ceramic
- DuraLith alkali aluminosilicate geopolymer
- FBSR granular product encapsulated within a geopolymer waste form.

Additional testing was performed in 2010 to further develop and optimize Cast Stone, DuraLith, and Ceramicrete for the projected liquid secondary waste compositions. Testing is also being conducted on an FBSR waste form. At the conclusion of this current development and optimization task, PNNL plans on testing each optimized waste form to demonstrate compliance with the IDF criteria to support the final waste form selection. Part of that testing includes engineering-scale demonstrations of the DuraLith and Ceramicrete waste form processes and characterization of the resulting engineering-scale waste form products.

1.3 Secondary Waste Form Down-Selection Data Package Content

In defining the content to be provided in the waste form down-selection data packages, previous waste form selection processes at the Hanford Site were examined. In 2002, DOE implemented a plan to accelerate the cleanup of the Hanford Site. Part of that plan was to conduct supplemental tank waste processing external to the WTP. Three waste form technologies (containerized grout, bulk vitrification, and fluidized-bed steam reforming) were considered (Raymond et al. 2004). A selection criteria workshop and follow-up meetings were conducted with DOE, Ecology, the U.S. Environmental Protection Agency (EPA), and contractor management and technical staff. Through that process 6 treatment goals, 10 selection criteria, and 14 measures were identified to aid in selecting the supplemental waste form. These are shown in Table 1.1.

Also to support the supplemental treatment waste form evaluation, Josephson et al. (2003) identified laboratory and engineering data needed to address the goals, selection criteria, and measures for the down-selection. Specific recommendations were provided for the containerized grout and the bulk vitrification options. Table 1.2. Summary of Testing Recommendations for Containerized Grout Technology—Waste Form Performance(a)

Technical Issue/Uncertainty	Testing Objective
Data on nitrate/nitrite and Cr release rates from test samples to meet performance assessment (PA) data needs	Optimize grout formulation to provide highest waste loading with lowest release rate. Performance on nitrate/nitrite likely to be limiting factor on waste loading. Determine waste loading/performance relationship (until a target for release is set, the relationship is more important than determining a waste loading that meets a criterion.)
Retention of Tc, U, and I as a function of waste loading	Gather enough Tc, U, and I release data to meet PA data needs. Determine waste loading/performance relationship (until a target for release rate is set, the relationship is more important than determining a waste loading that meets a criterion.)
Identification of constituents that might be poorly retained by grout and may impact permitting	Determine other key risk drivers and make suitable measurements to support calculations/models. RCRA metals, other radionuclides (e.g., Cs), all listed waste constituents (series of codes for solvents F001-F005), Land Disposal Restrictions (LDR) organics and inorganics, and criteria metrics-fish bioassay.
Validity of simulant testing	Demonstrate that simulant and actual waste release rates match. Verify that solidification materials locally available at the Hanford Site produce desired results.
Effects of mitigating features on environmental performance	Determine efficacy of proposed "getters." Determine efficacy of mitigating features for preventing contaminants from leaving the disposal system. Estimate expected efficacy of proposed feature for long-term Hanford application.
Data to support grout facility design	Collect grout curing and strength data. Collect data on H_2 generation in container. Collect data on amount of leachate generated as grout cures (or use existing data with engineering analysis if sufficient to address issue).

(a) Josephson et al. 2003

lists the technical issues and uncertainties and the testing objectives that should be addressed to resolve the identified issues and uncertainties for the containerized grout technology.

Types of data were identified to address each of the goals, criterion, and measures developed for the supplemental treatment down-selection and the technical issues/uncertainties and testing

recommended for the containerized grout. Appendix A includes expanded versions of Table 1.1 and Table 1.2. Summary of Testing Recommendations for Containerized Grout Technology—Waste Form Performance[(a)]

Technical Issue/Uncertainty	Testing Objective
Data on nitrate/nitrite and Cr release rates from test samples to meet performance assessment (PA) data needs	Optimize grout formulation to provide highest waste loading with lowest release rate. Performance on nitrate/nitrite likely to be limiting factor on waste loading. Determine waste loading/performance relationship (until a target for release is set, the relationship is more important than determining a waste loading that meets a criterion.)
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(a) Josephson et al. 2003

with the data package contents to address each measure and testing objective.

1.4 IDF Waste Acceptance Criteria

Wastes intended for disposal in IDF must meet requirements of DOE Order 435.1 and permit requirements established by Ecology. The IDF permit does not identify specific waste acceptance criteria for solidified secondary wastes. It does require that "Six months prior to IDF operations, Permittees shall submit to Ecology for review, approval, and incorporation into the permit, all waste acceptance criteria to address at a minimum, the following: physical/chemical criteria, liquids and liquid containing waste, land disposal restriction treatment standards and prohibitions, compatibility of waste with liner, gas generation, packaging, handling of packages, minimization of subsidence."

IDF waste acceptance criteria have not been established for wastes to be disposed of in the facility. There have been several draft proposed waste acceptance criteria, some limited to the ILAW glass waste form and the bulk vitrification waste form. Others have included criteria applicable to other waste forms as well (RPP 2005). Appendix B lists initial draft waste acceptance criteria for a secondary waste form based on the February 2005 draft IDF waste acceptance criteria (Burbank 2005) and the data package content to address each criterion. Included are criteria with respect to free liquids, compliance with land disposal restrictions, compressive strength, and leachability. For the purposes of the secondary waste form down-selection, the following requirements apply:

- Land Disposal Restrictions: The waste form will meet the land disposal requirements in 40 CFR 268 by meeting the Universal Treatment Standards (UTS) in Title 40 Part 268.48 of the Code of Federal Regulations (CFR) via the Toxicity Characteristic Leach Procedure (TCLP) test (EPA 2000).

Table 1.1. Supplemental Treatment Technology Selection Decision Goals, Criteria, and Measures[(a)]

Goal	Criterion	Measures
Ensure worker and public safety	Achieve inherently safe system	Independent safety expert assessment
Provide environmental protection comparable to current vitrified waste disposal plan	Waste form performance	Flux at points of undisturbed soil and bottom of the waste packages
	Disposal space required	Acres of land for disposal site
	Secondary wastes produced	Potential to emit (PTE) constituents: solid waste volume, liquid waste volume
Maximize schedule acceleration	Confidence in meeting 2028 date	50% probability data for achieving 10 gpm throughput
	Process robustness	Metric tons of sodium (Na) processed by 2028
Maximize cost effectiveness	Life cycle cost	Life cycle cost
	Peak year cost	Peak year cost
Maximize operability	Operability risk	Independent expert assessment to include number of unit operations, equipment count, etc.
Minimize overall system interface impacts	System interface impacts	Liquid effluent greater than ETF capacity
		Dose of waste package (impacting handling within disposal system
		Volume returned to double-shell tanks (DSTs) (impacting stored waste volume)

(a) Raymond et al. 2004

Table 1.2. Summary of Testing Recommendations for Containerized Grout Technology—Waste Form Performance[(a)]

Technical Issue/Uncertainty	Testing Objective
Data on nitrate/nitrite and Cr release rates from test samples to meet performance assessment (PA) data needs	Optimize grout formulation to provide highest waste loading with lowest release rate. Performance on nitrate/nitrite likely to be limiting factor on waste loading. Determine waste loading/performance relationship (until a target for release is set, the relationship is more important than determining a waste loading that meets a criterion.)
Retention of Tc, U, and I as a function of waste loading	Gather enough Tc, U, and I release data to meet PA data needs. Determine waste loading/performance relationship (until a target for release rate is set, the relationship is more important than determining a waste loading that meets a criterion.)
Identification of constituents that might be poorly retained by grout and may impact permitting	Determine other key risk drivers and make suitable measurements to support calculations/models. RCRA metals, other radionuclides (e.g., Cs), all listed waste constituents (series of codes for solvents F001-F005), Land Disposal Restrictions (LDR) organics and inorganics, and criteria metrics-fish bioassay.
Validity of simulant testing	Demonstrate that simulant and actual waste release rates match. Verify that solidification materials locally available at the Hanford Site produce desired results.
Effects of mitigating features on environmental performance	Determine efficacy of proposed "getters." Determine efficacy of mitigating features for preventing contaminants from leaving the disposal system. Estimate expected efficacy of proposed feature for long-term Hanford application.
Data to support grout facility design	Collect grout curing and strength data. Collect data on H_2 generation in container. Collect data on amount of leachate generated as grout cures (or use existing data with engineering analysis if sufficient to address issue).

(a) Josephson et al. 2003

- Free Liquids: The waste form shall contain no detectable free liquids as defined in SW-846 Method 9095.
- Leachability Index (LI): The waste form shall have a sodium LI greater than 6.0 when tested in deionized water using the American National Standards Institute/American Nuclear Society (ANSI/ANS)-16.1 method or EPA Method 1315 (EPA 2009c). The waste form shall have a rhenium or technetium LI greater than 9.0 and LI exceeding 11.0 for ^{129}I. These requirements are based on the Nuclear Regulatory Commission's *Technical Position on Waste Form* (NRC 1991) and on early waste disposal risk assessments and performance assessment (PA) analyses. The stated values need

to be validated and verified based on future risk assessments and PA analyses. It is anticipated that future PA analyses will address and bound long-term durability issues for the stabilized secondary waste from, package and overall IDF disposal system.

- Compressive Strength: The compressive strength of the waste form shall be at least 3.54E6 Pa (500 psi) when tested in accordance with ASTM International [formerly the American Society for Testing and Materials] (ASTM) C39/C39M. This is based on the Nuclear Regulatory Commission's (NRC's) *Technical Position on Waste Form* (NRC 1991), which is more restrictive for cement-based waste forms.

1.5 Data Package Content

The data package begins with a description of the waste form in Section 2. This includes the primary waste form, any encapsulating materials, the waste form packaging, and the types of wastes tested. Section 3 describes the waste form preparation process, including starting materials and processing steps. Section 4 expands upon the information in Section 3 to include flowsheet and equipment descriptions, process control, off-gas treatment and process effluents, and any existing test and production facilities. Physical properties of the waste form are presented in Section 5. Section 6 focuses on waste form performance, including leach test results and mechanisms of radionuclide and hazardous chemical containment and release. Data that address specific IDF waste acceptance criteria are provided in Section 7. Section 8 concludes with a summary of the strengths and weaknesses of the waste form.

2.0 Waste Form Description

DuraLith is a geopolymer-based waste form. Most of the geopolymers are made from alkali activation of aluminosilicates, although acid phosphate-activated, metal oxide geopolymers are also known to exist. The earliest study on geopolymerization involving alkali-activated, blast furnace slag was published by Purdon (1940). In the 1970s, additional studies were conducted by Glukhovsky and others on alkali activation of slags. These investigators identified the products of geopolymerization reaction to be calcium silicate hydrates and calcium and sodium aluminosilicates (Glukhovsky et al. 1980). Later, Davidovits and Sawyer (1985) obtained a patent that described the materials (clay, slag, fly ash, pozzalan, and alkali) and methods of making geopolymer materials under low temperature (<160°C) conditions.

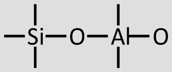
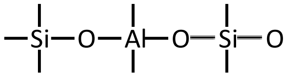
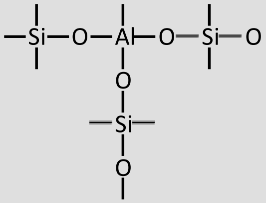
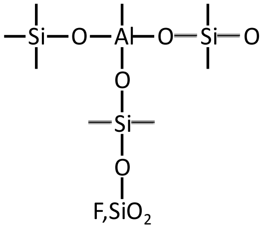
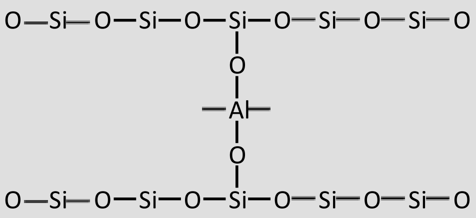
The aluminosilicate source materials for geopolymer production typically consist of alumina and silica mix, metakaolin, blast furnace slag, and fly ash. These may be used separately in some specific combinations before adding caustic solution. The geopolymers are broadly classified as follows (Davidovits 2008):

- Kaolinite/hydrosodalite polysialates
- Metakaolin MK-750, poly sialate-silaxo type
- Calcium, potassium, sodium sialates
- Silicate rock based polysialate-multisilaxo type
- Silica based polysilaxonates
- Fly ash based geopolymers
- Phosphate-based geopolymers
- Organic-mineral geopolymers.

The uses of various geopolymers as a function of their composition (Si to Al Ratio) are listed in Table 2.1. The silica-to-alumina ratio of the starting materials dictates the resulting geopolymer structure and its potential use. At equimolar silica-to-alumina ratio, the resulting polysialate structures consist of a rigid 3D network. With increasing silica in the mix, linear polymeric structures develop that contain polysialate bonds and an increasing degree of silaxo, disilaxo, and polysilaxo bonds. At very high silica-to-alumina ratios (20:1 to 35:1), the resulting polymeric structures are predominantly polysiloxates with properties suitable for use in fire-resistant composites. A silica-to-alumina ratio of 2:1 has been suggested for geopolymers intended for radioactive and toxic waste encapsulation applications. A typical compositional (Si:Al ratio) and temperature range to produce geopolymer (Davidovits 2008) is shown in Figure 2.1. As compared to feldspars and zeolites, the geopolymers form under relatively lower temperature conditions.

A literature review was conducted to identify geopolymer research that is relevant to encapsulate toxic and radioactive wastes. The results of this review have been tabulated in Table 2.2.

Table 2.1. Silica-to-Alumina Ratios, Bond Types, and Applications of Geopolymers[(a)]

Si:Al Ratio	Types of Polymeric Bonds	Low Technology Applications	High Technology Applications
1:1	 Polysialate	Bricks, Ceramics	Fire protection
2:1	 Polysialate-silaxo	Low CO_2 cements and concretes	Radioactive and toxic waste encapsulation
3:1	 Polysialate-disilaxo	Fiber glass composites, foundry equipment	Titanium processing toolings
>3:1	 Polysialate-polysilaxo	Industrial sealants (200 – 600 ºC)	aluminum toolings
20:1 to 35:1	 Sialate-polysilaxo	--	Fire and heat resistant composites

(a) Davidovits 2008.

Table 2.2. Categorization of Geopolymer Literature

Category	References
Effects of components and additives on geopolymer synthesis	Brew et al. 2007; Duxson et al. 2005b,d,e,f; 2007; Fletcher et al. 2005; Glukhovsky et al. 1980; Keyte et al. 2004; Kumar et al. 2010; Lee and Van Deventer 2000a,b; 2001; 2002a,b,c,e; Luz Granizo et al. 2007; Phair et al. 1999, 2000b, 2002a, 2004; Rees et al. 2004; Rowles and Conner 2003; Van Jaarsveld and Van Deventer 1999a,b,c, e; Van Jaarsveld et al. 2002, 2003, 2004; Xu and Van Deventer 1999, 2003; Xu et al. 2004; Yip and Deventer 2001, 2002a,b; Yip et al. 2003a
Geopolymer formation reactions, kinetics and mechanisms	Buchwald et al. 2009; Chen et al. 2011a,b; Khale and Chaudhary 2007; Lee et al. 1999; Lee and Van Deventer 2002e; Provis et al. 2005a; Provis and Van Deventer 2004a,b; 2007a,b,c; Provis and Van Deventer and Lukey 2005a; Sagoe-Crentsil and Weng 2007; Sindhunata et al. 2004, 2006; Weng and Sagoe-Crentsil 2007; Xu and Van Deventer 2000b, 2002; Zhang et al. 2009; Zheng et al. 2000
Geopolymer structural ordering, spectroscopic and microscopic analysis and modeling	Duxson et al. 2005a; 2005c,e, 2006c,d; Lee and Van Deventer 2002d; 2003; Lloyd et al. 2009a,b; Phair et al. Phair and Van Deventer 2002b; Provis et al. 2004a; Provis and Deventer 2004a,b, Provis et al. 2005b,c,d,e,f,g; Provis and Van Deventer 2007a,b,c; Singh et al. 2005; Xu and Van Deventer 2000a,b,c; Xu et al. 2003; Yip and Deventer, 2003, 2005; Yip et al. 2003b
Methods of Geopolymer synthesis	Davidovits 1993; Davidovits et al. 1993; Feng et al. 2004.
Geopolymer use as stable waste forms for radionuclide and metallic contaminants	Gong et al. 2010; Davidovits 1994; Lorenzen et al. 1996; Phair et al. 2000a; Van Jaarsveld et al. 1996a,b,c; 1997a,b, 1998, 1999; Van Jaarsveld and Van Deventer 1999c,d
Thermal properties of geopolymers: Heat evolution, stability, conductivity	Duxson et al. 2003; 2006a,b

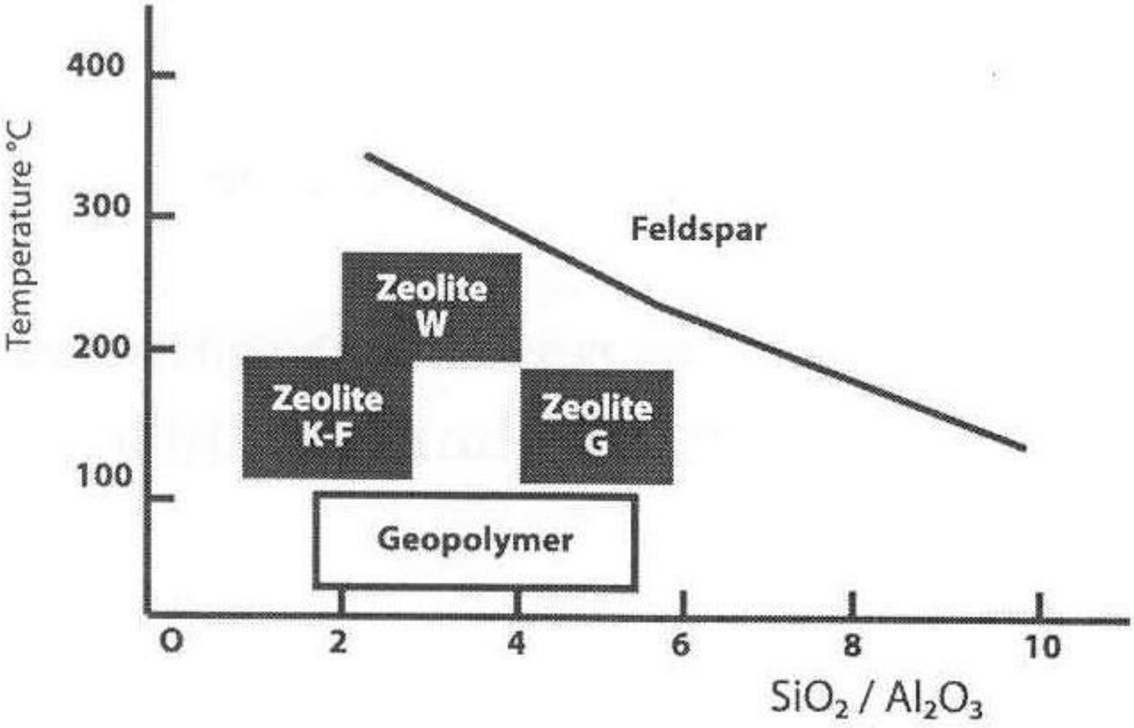


Figure 2.1. Temperature and Compositional Ranges for Geopolymer Formation (Davidovits 2002)

2.1 Primary Waste Form

Based on a review of potential candidate waste stabilization technologies for Hanford liquid and solid secondary waste, Pierce et al. (2010a) identified DuraLith geopolymer as one of the waste forms that needs further evaluation. DuraLith is an alkali-activated mixture of metakaolinite and blast furnace slag (Gong et al. 2010). Some amount of sand is used as a filler material. First the alkalis (potassium hydroxide and sodium hydroxide) and silica fume[1] are added to the liquid waste to produce an activator solution. Next, the activator solution is blended into the dry ingredient mixture to initiate polymeric reactions. A small amount of tin (II) chloride or fluoride is added to reduce Tc(VII) into less soluble Tc(IV), and silver zeolite is added to precipitate radioiodine. A set of optimized DuraLith monoliths prepared by Gong et al. (2006, 2011) using Hanford secondary waste (HSW) simulants is shown in Figure 2.2 and Figure 2.3.

2.1.1 Chemical Composition

DuraLith compositions have been optimized for each waste type so that the monoliths meet the appropriate waste acceptance criteria. In 2006, the DuraLith compositions were optimized for HSW and Idaho Sodium-bearing Waste (SBW) (Gong et al. 2006). DuraLith monoliths prepared with a Hanford secondary waste simulant were tested by Pierce et al. (2010b), and later optimization tests were conducted for the Hanford secondary waste simulants S1 to S4 (Gong et al. 2011). The DuraLith compositions used

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[1] Silica fume is a byproduct in the production of high-purity quartz , silicon, and ferrosilicon alloys.

for incorporating these various wastes are listed in Table 2.3. This table shows the evolution of the DuraLith compositions from 2006 to 2011 in terms of the relative proportions of various ingredients, the use of new ingredients such as sand, sodium hydroxide, silver zeolite, water reducer, copper slag, and tin compounds, and the elimination of additives, such as gypsum, super plasticizers, and sodium sulfide.

Figure 2.2. DuraLith Monoliths Optimized for Hanford Secondary Wastes (Gong et al. 2006)

Figure 2.3. DuraLith Monoliths Optimized for Hanford Secondary Wastes (Gong et al. 2011)

Table 2.3. Optimized DuraLith Compositions

	HSW(a)		SBW(a)	WTP Waste Simulant(b)	HSW S1 Simulant(c)		HSW S4 Simulant(c)	
	TB9-4	TB9-1R	ED-SA3	Batch 1&2	S1-6X1R FS	S1-6X2R MK	S4-6X1 FS	S4-6X2 MK
Ingredients	wt%							
Metakaolin	13.88	12.52	10.81	21.26	11.47	20.25	9.80	16.99
Blast Furnace Slag	35.69	32.18	27.23	13.96	29.60	13.86	25.28	11.62
Silica Fume	11.73	10.33	9.82	12.12	8.98	12.22	7.28	9.47
K_2O	9.53	6.29	11.55	10.75	4.44	7.83	4.63	8.04
Na_2O	--	--	--	0.53	2.15	0.97	1.90	0.87
Sand	--	--	--	19.85	19.20	19.35	19.00	19.00
Waste Simulant	28.44	37.58	30.30	20.87	23.15	24.50	29.11	31.01
Gypsum	0.73	1.10	1.53	--	--	--	--	--
Super Plasticizer	--	--	0.49	--	--	--	--	--
Tin Chloride/Fluoride	(d)	(d)	(d)	--	(e)	(e)	(e)	(e)
Copper Slag	--	--	--	--	--	--	2.00	2.00
Water Reducer	--	--	--	--	(d)	(d)	--	--
$AgNO_3$/Ag mordenite	(d)	(d)	(d)	0.52	1.01	1.02	1.00	1.00
Sodium sulfide	--	--	--	0.13	--	--	--	--

(a) Gong et al. 2006.
(b) Pierce et al. 2010b.
(c) Gong et al. 2011.
(d) Trace quantities.
(e) Tin fluoride.
Water Reducer: ADVA 140 M.

The DuraLith compositions have evolved since their initial formulations in 2006. For instance, the most recent optimized compositions have reduced the blast furnace slag (BFS) content with sand added as filler material. A small amount (1% to 2%) of sodium hydroxide is part of the newer DuraLith formulation. Previously recommended additives, such as a superplasticizer, gypsum, and sodium sulfide, have been left out of the current formulation. Other changes include substituting tin fluoride for tin chloride and adding small quantities (≤1%) of a water-reducing compound, ADVA 140M, and about 1% of silver mordenite. One of two of the recent formulations (S1-6X1R FS) optimized for 6 M Na–S1 simulant is BFS rich (~30%), whereas the second (S1-6X2R MK) has a higher metakaolin content (20%). The preferred formulation is S1-6X1R FS because it is less expensive to formulate (metakaolin costs more than BFS) and also evolves less heat generation during alkali activation (Gong et al. 2011)

2.1.2 Composition of DuraLith Ingredients and the Waste Forms

The detailed chemical analysis of DuraLith ingredients and the monoliths made with secondary waste simulant were provided by Pierce et al. (2010b). These are listed in Table 2.4. The data show that a part of the total amount of some RCRA metals contained in DuraLith monoliths originate from the ingredients. About 46.8 wt% of cadmium in the monoliths originates from the simulant and the remaining quantity originates from fume silica (9.5 wt%), metakaolin (16.7 wt%), furnace slag (11.0 wt%), sand (15.6 wt%), and Ag-zeolite (0.4 wt%). Meta-kaolinite is the largest single source of chromium, and it contributes ~ 76.8 wt% of the total chromium in the monoliths. Fumed silica (7.0 wt%), simulant (8.6 wt%), sand (6.4 wt%), furnace slag (1.0 wt%), and Ag-zeolite (0.1 wt%) provide the remaining quantity of chromium. A significant source of lead in the monolith is the simulant (49.7 wt%) with remaining contributions originating from fumed silica (33.0 wt%), meta-kaolinite (6.8 wt%), furnace slag (4.2 wt%), sand (6.0 wt%), and Ag-zeolite (0.3 wt%). The source of silver in the monoliths is silver zeolite, and tin is from added tin fluoride that is added as a reductant to the Tc(VII) spike.

The analysis of the DuraLith ingredients used in optimization testing at the Vitreous State Laboratory (VSL) is listed in Table 2.5. Metakaolin is the major source of Al and Si. Silica Fume and sand (analysis not shown) are also sources of Si. Blast furnace slag is the source of Al, Ca, Mg, and Si. Copper slag is rich in Fe and Si. All the ingredients contain trace or undetectable quantities of As, Co, Cr, Mn, Mo, Pb, Pd, Rh, Tb, V, Zn, and Zr.

2.1.3 Mineralogy

X-ray diffraction (XRD) analysis conducted on TB9 samples (Gong et al. 2006) indicated that the monoliths were mainly amorphous, and the only crystalline component detected was calcium carbonate. It was hypothesized that calcium carbonate formation was the result of the reaction of the HSW simulant component, namely carbonate with calcium contained in the blast furnace slag. Scanning electron microscopic examination of the monolith showed two different morphologies. Irregularly shaped bright BFS particles (<20 to >50 µm) in size were embedded in a darker polymer matrix. Microcracks (20 to 100 µm long) were observed that terminated at particle boundaries. Pores 50 to 100 µm in size filled with fine grain material, presumably silica fume, were also visible.

Mineralogical analysis of the ED-SA3 sample showed two crystalline phases, Ca_2SiO_4 and Ca_3SiO_5 (Gong et al. 2006). The scanning electron microscopy (SEM) analysis of this monolith also showed irregularly shaped bright BFS particles (<20 to >50 µm) in size embedded in a darker polymer matrix.

Calcium silicate particles, some bright Fe_2O_3 particles, and presumably unreacted SiO_2 were also identified. Very fine pores and microcracks (20 to 100 µm long) were observed, and the cracks around some of the particles were attributed to probable shrinkage of particles during curing.

Table 2.4. Chemical Composition of DuraLith Ingredients and the Monoliths[(a)]

Elements	Silica Fume	Meta-Kaolinite	Blast Furnace Slag	Sand	Ag Zeolite	DuraLith Batch #1	DuraLith Batch #2
	Concentration (µg/g)						
Al	2.10E+02	3.67E+04	1.16E+01	3.34E+03	6.47E+03	6.76E+04	6.74E+04
Ag	--	--	--	--	--	1.01E+03	7.85E+02
As	4.00E+01	1.87E+01	3.46E+01	4.39E+01	2.16E+01	4.63E+00	1.06E+00
Ba	2.57E+01	1.32E+01	4.05E+01	7.01E+01	4.03E+00	2.07E+02	1.93E+02
Be	4.89E-01	<0.29	<0.27	<0.27	5.09E+00	--	--
Bi	<3.6	<3.6	<3.6	<3.6	<3.6	--	--
Ca	5.24E+03	<8.81	8.61E+03	1.64E+02	2.78E+02	5.35E+04	5.08E+04
Cd	<0.5	<0.5	<0.5	<0.5	<0.5	1.76E+00	1.84E+00
Co	<1.73	1.03E+01	<1.71	<1.71	<1.81	--	--
Cr	1.84E+01	1.16E+02	2.41E+00	1.04E+01	8.17E+00	2.59E+01	2.85E+01
Cu	2.05E+01	2.00E+01	<2.28	<2.28	<2.43	3.05E+00	3.36E+00
Fe	6.69E+02	1.93E+03	3.26E+02	3.87E+03	6.18E+03	2.34E+03	2.33E+03
Hg	--	--	--	--	--	1.90E+00	3.01E+00
I	--	--	--	--	--	<4.97E-01	<6.59E-01
K	4.58E+03	1.08E+03	2.83E+03	1.97E+03	4.86E+03	8.43E+04	7.91E+04
Li	1.22E+01	<7.89	3.08E+01	9.46E+00	<7.89	--	--
Mg	5.50E+02	7.02E+00	6.67E+02	5.16E+01	6.86E+00	1.13E+04	1.12E+04
Mn	2.36E+02	<0.76	4.07E+03	5.36E+01	5.85E+02	7.29E+02	7.34E+02
Mo	5.48E+00	3.24E+00	7.93E+00	9.17E+00	<2.88	--	--
Na	1.89E+03	1.61E+03	1.98E+03	1.50E+03	3.84E+03	1.92E+04	1.80E+04
Ni	<1.68	1.04E+01	<1.66	<1.66	<1.76	--	--
P	3.96E+02	8.94E+02	<10.55	5.36E+01	2.97E+02	4.81E+02	4.00E+02
Pb	3.22E+01	<3.80	<3.57	<3.57	6.67E+00	5.43E+01	5.06E+01
S	7.82E+02	2.05E+02	1.07E+04	4.50E+01	4.87E+01	1.88E+03	1.89E+03
Sb	2.16E+01	<8.43	<7.93	2.60E+01	<8.43	--	--
Se	<20.5	<20.5	<20.5	<20.5	<20.5	--	--
Si	4.02E+05	2.48E+05	1.84E+05	4.26E+05	2.90E+05	2.53E+05	2.45E+05
Sn	<4.4	<4.4	<4.4	<4.4	<4.4	8.19E+02	1.03E+03
Sr	5.33E+01	<0.55	2.36E+02	1.01E+01	1.11E+01	2.11E+02	1.96E+02
Tc	--	--	--	--	--	3.01E-01	2.29E-01
Ti	3.02E+01	1.09E+04	2.97E+03	2.43E+03	7.29E+02	4.08E+03	4.00E+03
Tl	<11.61	1.50E+02	2.00E+01	4.94E+01	6.26E+01	--	--
U	<2.63	2.61E+01	<2.59	<2.59	<2.76	--	--
V	2.60E+00	1.68E+02	2.41E+01	1.23E+01	1.52E+01	3.11E+00	2.05E+01
Zn	7.67E+02	3.03E+01	1.36E+01	1.15E+01	1.51E+02	1.51E+02	1.39E+02
Zr	1.24E+01	1.05E+02	2.54E+01	8.99E+01	1.15E+02	1.04E+02	1.23E+02

(a) Pierce et al. (2010b).

Table 2.5. Chemical Composition of DuraLith Ingredients(a)

Elemental Oxide Basis	Ag-Zeolite	Blast Furnace Slag	Metakaolin			Silica Fume	Copper Slag
Source	Molecular Products	Lafarge	Thiele		Advanced Cement Technologies	Norchem	Opta Minerals
	wt%						
Ag_2O	53.6	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01
Al_2O_3	9.62	9.02	42.78	42.99	40.04	0.34	4.48
BaO	<0.01	0.07	0.01	<0.01	0.04	<0.01	0.06
CaO	0.92	36.73	0.03	0.01	0.04	0.86	1.87
Cl	<0.01	0.02	0.01	<0.01	<0.01	0.05	<0.01
Cr_2O_3	<0.01	<0.01	0.03	0.02	0.02	<0.01	0.09
CuO	<0.01	<0.01	0.01	0.01	<0.01	0.01	1.37
Fe_2O_3	1.32	0.35	0.53	0.42	2.08	0.73	53.31
K_2O	0.58	0.38	0.18	0.19	0.26	0.73	1.58
MgO	1.88	12.17	<0.01	<0.01	<0.01	0.45	1.17
MnO	0.09	0.5	<0.01	<0.01	<0.01	0.09	0.07
Na_2O	0.33	0.27	0.24	0.27	<0.01	0	0.42
P_2O_5	0.17	<0.01	0.27	0.09	0.22	0.13	0.13
PbO	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	0.14
PdO	0.05	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01
Rh_2O_3	0.02	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01
S	<0.01	1.28	<0.01	<0.01	<0.01	<0.01	0.48
SO_3	<0.01	<0.01	0.08	0.11	0.04	0.24	<0.01
SiO_2	59.76	38.61	53.74	54.01	55.49	93.88	33.13
SrO	<0.01	0.08	<0.01	0.01	0.01	<0.01	0.02
TiO_2	0.17	0.49	2.07	1.83	1.7	<0.01	0.34
V_2O_5	<0.01	<0.01	0.03	0.03	0.02	<0.01	0.01
ZnO	0.01	<0.01	<0.01	<0.01	0.01	0.04	0.79
ZrO_2	0.03	0.03	<0.01	0.01	0.02	0	0.02
Sum	100	100	100	100	100	97.58(b)	99.48(c)

(a) Gong et al. (2011).
(b) 2.42% carbon.
(c) Containing additional 0.12 wt% As_2O_5, 0.08 wt% CoO, 0.25 wt% MoO_3, and 0.07 wt% Tb_4O_7.

Powder XRD of ingredients and the resulting DuraLith monoliths were conducted by Pierce et al. (2010b) as part of Phase I testing of secondary waste forms. The silica fume was mainly amorphous with detectable amounts of crystalline components, such as quartz and silicon carbide. Metakaolinite was also amorphous but contained trace amounts of 10Å halloysite and anatase. The BFS was amorphous, and sand was mainly crystalline quartz and tridymite with a small amount of amorphous component. The silver zeolite consisted of two crystalline phases, namely mordenite and Na-heulandite. The cured DuraLith sample was mainly amorphous with <26% by wt crystalline component identified to be quartz.

The scanning electron microscopy-energy dispersive spectrometry (SEM-EDS) analysis of the DuraLith monolith confirmed through elemental associations and morphologies the presence of metakaolinite, halloysite, and Ag-zeolite in a largely amorphous matrix.

2.1.4 Getters

Getters are most commonly inorganic materials that selectively adsorb radionuclide and metallic contaminants. Blast furnace slag is one of the principal components of the DuraLith polymeric waste form. BFS can act as a getter because it has been demonstrated to reduce Tc(VII) release through reduction (Aloy et al. 2007; Gilliam et al. 1988, 1990; Kaplan et al. 2008; Langton 1988a,b; NRC 2001; Spence and Shi 2005). Depending on the source, BFS has reductive capacities that range from 0.82 to 4.79 meq/g (Aloy et al. 2007; Kaplan et al. 2008; Lukens et al. 2005). Test data indicate that unless protected from oxygen intrusion, the BFS getter-based waste forms tend to release Tc (VII) by oxidation of Tc_2S_7 (Aloy et al. 2007; Lukens et al. 2005).

Another component used in DuraLith formulation is Ag-zeolite, which has been historically used as a radioiodine getter (Pierce et al. 2010a). Although silver mordenite had an acceptable Toxicity Characteristic Leach Procedure (TCLP) release from a well-designed cementitious waste form (Scheele et al. 1984, 2002), at present it is unknown whether direct land disposal of grouted spent silver zeolite would be acceptable because of the potential variability in its chemical composition. The long-term leachability of silver from the DuraLith waste form needs to be studied.

2.1.5 Reductants

During various studies, sodium sulfide, tin(II) chloride, and tin (II) fluoride have been recommended as a reductant for Tc(VII) in the DuraLith waste form (see Section 2.1). Tin (II) compounds are known to reduce Tc(VII) to Tc(IV) that precipitates out into a limited solubility compound, TcO_2 $2H_2O$, thus reducing its leaching potential. Similarly, Na_2S, upon reacting with Tc(VII), is known to reduce and precipitate $TcO_2 \cdot 2H_2O$ and also precipitate Tc_2S_7 without reduction (Shuh et al. 2002; Um et al. 2011). Although these Tc compounds have low solubility, thus limiting the leaching of Tc from the waste form, oxygen intrusion may reoxidize Tc(IV) and sulfide, thus engendering the release of Tc(VII).

2.2 Waste Form Container/Package

The waste form container/package provides both protection and containment for the waste form during production, transportation, and storage before final disposal in a subsurface repository. A waste form container or package has not been selected for the DuraLith waste form for WTP secondary wastes. The waste form container will need to meet requirements for transporting radioactive and hazardous materials as specified in 49 CFR 173. The materials of construction for the package must be compatible with the wastes and with the protective liners included in the IDF design. Generally, the package will be fabricated using one or a combination of the following materials, which are acceptable to the IDF:

- Metal, concrete, masonry
- Fire-retardant-treated or painted wood

- Rigid plastic with a maximum flame-spread rating or coating of 25
- Flexible plastic packaging materials with similar flame-spread characteristics.

The size of the container will be dictated by criticality safety considerations. A criticality safety evaluation for the IDF qualified the following container sizes:

- 55-gallon (208 L, 0.21 m^3) drums, 57.15 cm diameter × 88.14 cm high (22.5 inches in diameter × 34.7 inches high)
- 85-gallon (322 L, 0.32 m^3) drums, 66 cm diameter × 100.3 cm high (26 inches in diameter × 39.5 inches high)
- MB-V boxes, 1.2 m wide × 1.2 m high × 2.4 m long (4 ft wide × 4 ft high × 8 ft long)
- Medium boxes with a volume between 3.95 m^3 (5.17 yd^3) and 15 m^3 (19.62 yd^3). The dimensions are not fixed.
- Small boxes with a volume less than 3.95 m^3 (5.17 yd^3). The dimensions are not fixed.

Other container configurations may be acceptable but would require a criticality safety evaluation. The size of the container will also be constrained by waste form processing and curing considerations. Any elevated temperatures of the waste form slurry as it is poured into the container will need to be dissipated as will any heat generated by the curing processes for the waste form. The container will need to be sized and filled such that the heat dissipates without impacting the quality of the waste form.

The container will also be configured for ease of filling to maximize the volume of waste form to meet minimum fill requirements and to minimize void spaces. The flow and curing characteristics of the waste form are important considerations in maximizing the fill volume.

The packages will be configured with the appurtenances necessary for safe handling, lifting, and transporting. Appropriate markings and labels will be permanently attached to each package.

2.3 Range of Wastes and Compositions Tested for DuraLith

The compositions of Hanford secondary wastes that were tested in 2005 and 2010 and that of Idaho sodium-bearing waste tested previously in 2005 are described in the following sections.

2.3.1 Composition of Wastes

The DuraLith formulations have been optimized for a range of liquid wastes, including HSWs and Idaho SBWs. The compositions of HSWs and SBWs that were tested during the years 2005 to 2006 are listed in Table 2.6 and Table 2.7. The HSW simulant was mainly an ~2 M sodium carbonate solution with minor concentrations of nitrate, hydroxyl, and total organic carbon (TOC) and trace concentrations of Ag, Cr, Cd, I Re(Tc), Hg, and Pb. The Idaho SBW was an acidic ~1.9 M sodium nitrate solution with other minor and trace constituents (Table 2.7).

Table 2.6. Composition of WTP HSW Waste Used for DuraLith Formulation

Element	Target (Molar)	Target (g/L)	Analysis (g/L)
Na	2	46	45.17
Al	0.011	0.299	0.318
Cr	2.80E-04	0.0145	0.0149
Ag	2.20E-04	0.0237	0.0235
Cd	1.40E-05	0.00157	0.00157
Re (Tc)	6.00E-07	1.12E-04	1.25E-04
I	2.90E-06	3.68E-04	NA
Hg	2.40E-06	4.81E-04	4.15E-04
Pb	1.50E-04	0.031	0.0323
CO_3^-	0.96	57.6	60
NO_3^-	0.018	1.116	1.12
OH^-	0.094	1.598	1.6
TOC	0.18	13.86	13.86

All analyses were conducted by Noah Laboratory, except the Re(Tc) analysis, which was conducted by Argonne Laboratory, Chicago, Illinois.
NA = Not analyzed.
Reference – Russell et al. (2006).

Table 2.7. Composition of Idaho SBW Waste Used for DuraLith Formulation

Element	Target (moles/L)	Target (g/L)	Analysis (g/L)	Element	Target (moles/L)	Target (g/L)	Analysis (g/L)
Na	1.88	43.24	43.2	Ce	5.30E-06	7.43E-04	7.82E-04
Al	0.575	15.5	17.8	Hg	0.002	0.401	0.4
Ca	0.0366	1.464	1.46	Pb	0.0013	0.269	0.27
B	0.0102	0.11	0.11	Re (Tc)	3.13E-06	5.83E-04	6.37E-04
Mg	0.0108	0.26	0.26	I	5.66E-05	7.18E-03	3.43E-03
K	0.175	6.825	6.8	SO_4^-	0.0491	4.71	5.15
Cr	0.0033	0.172	0.172	H_2O	45.1	812.7	812
Mn	0.0126	0.69	0.69	NO_3^-	4.91	304.4	269
Fe	0.0178	0.993	0.99	F	0.0403	0.765	0.83
Cd	0.0007	0.0786	0.078	Cl	0.0285	1.009	1.15
Cs	7.99E-10	1.10E-07	2.34E-05	H	1.87	1.87	NA

All analyses were conducted by Noah Laboratory, except the Cs, Ce, I, Re(Tc) SO_4, NO_3, F, and Cl analysis, which was conducted by Argonne Laboratory, Chicago, Illinois.
NA = Not analyzed.
Reference – Russell et al. (2006).

The liquid secondary waste simulant composition used for DuraLith formulation for Phase I testing (Table 2.8) was developed using flow sheet model simulations of the WTP process (Pierce et al. 2010b). The target composition was adapted from an analysis of a G2 flowsheet model run (MRQ 09-0019 Scenario 5.0.22a, Node RLD-TK- 00006B_ETF-1). The model node for the baseline case (caustic scrubber) is for the process condensate collection tank (RLD-06B) that holds the liquid wastes to be sent to the Liquid Effluent Retention Facility (LERF)/ETF. In totalizer mode, the model provides the composition of the liquid residing in the RLD-06B tank on a monthly basis. For developing the target simulant concentration, the predicted monthly concentrations were first normalized to 2 M Na and then averaged over 241 months. After averaging, it was necessary to increase the amount of sodium to provide a charge balance based on the averaged estimates of NO_3^- CO_3^{2-}, PO_4^{3-} andSO_4^{2-}. Concentrations of silver, cadmium, and lead were increased so as to be analytically detectable. The technetium concentration in the simulant was set at its maximum expected concentration.

Table 2.8. Composition of WTP Secondary Waste Simulant

Element	Target (Molar)[a]
Na	2
Al	0.23
Cr	3.70E-04
Ag	2.50E-04 (100×)
Cd	5.00E-05 (100×)
^{99}Tc	7.70E-06[b]
I	2.90E-06
Hg	3.30E-06
Pb	7.90E-04 (100×)
CO_3^-	1.50E-06
NO_3^-	0.69
OH^-	1.2
PO_4	1.70E-02
SO_4	9.70E-03
TOC (as oxalate)	0.18

(a) Adopted from Melvin (2009).
Reference – Pierce et al. (2010b).
(b) ^{99}Tc = 1.30E-05 Ci/L.

The baseline waste composition of simulant S1 used for optimizing the DuraLith composition is listed in Table 2.9 (Gong et al. 2011). These optimizations were conducted using 4×, 5×, 6×, 8×, and 12× of the baseline concentrations to explore a range of waste loadings. The baseline composition of S4 simulant is listed in Table 2.10. Optimizing the DuraLith formulations increased the waste loading for S4 simulant, which was carried out by using 4× and 6× of the baseline concentrations. These optimized DuraLith formulations used Re as a surrogate for Tc.

Table 2.9. Baseline Composition of WTP Secondary Waste S1

Component	Baseline Conc (Molar)	Component	Baseline Conc (Molar)
Na	1	F-	5.57E-04
$Al(OH)_3$	9.39E-02	Cr	2.03E-04
Si	1.88E-03	Ag	6.27E-06
K	5.82E-04	As	3.48E-05
OH-	3.98E-01	Cd	1.57E-06
$NO_3{}^-$	3.28E-01	Hg	1.13E-05
$CO_3{}^{-2}$	2.28E-02	Pb	8.99E-06
Cl^-	2.25E-02	Tc[(a)]	1.81E-05
$NO_2{}^-$	1.20E-02	I	4.62E-06
$PO_4{}^{-3}$	6.87E-03	TOC	9.39E-02
$SO_4{}^{-2}$	4.41E-03	Re	3.62E-04

(a) Not used.

Table 2.10. Baseline Composition of WTP Secondary Waste S4

Component	Baseline Conc (Molar)	Component	Baseline Conc (Molar)
Na	1	F^-	1.02E-08
Al(OH)3	4.24E-02	Cr	1.09E-03
Si	1.39E-02	Ag	2.35E-05
K	2.87E-02	As	1.61E-05
OH-	1.04E-08	Cd	2.16E-06
$NO_3{}^-$	1.13E-00	Hg	5.30E-06
$CO_3{}^{-2}$	1.04E-02	Pb	8.28E-06
Cl^-	1.04E-02	Tc[(a)]	5.59E-04
$NO_2{}^-$	4.31E-02	I	6.29E-05
$PO_4{}^{-3}$	5.10E-03	TOC	4.24E-02
$SO_4{}^{-2}$	4.36E-02	Re	2.51E-04

(a) Not used in DuraLith formulations.

2.3.2 Waste Loading and Sodium Molarity

The waste loadings achieved on the solid basis during the DuraLith formula optimization are listed in Table 2.11. Using concentrated (~4 M Na) WTP secondary waste (2005 composition), waste loadings as high as ~5.75 by mass were achieved for the TB9 waste form series (Gong et al. 2006). For SBW, the acidic simulant (~1.9 M Na) was neutralized with CaO and/or ordinary Portland cement (OPC), resulting in a waste loading of ~9% by weight. Recently, the same investigators (Gong et al. 2011) achieved solid waste loading ranging from ~7% to 8% using 6 M Na waste simulants (Hanford S1 secondary waste). Comparatively, using 2 M Na HSW S1 waste resulted in a waste loading of ~3% by weight (Pierce et al. 2010b).

Based on these data, it is feasible to achieve a maximum solid waste loading of 7% to 8% by mass using a more concentrated S1 HSW (S1). Similarly, using 6 M Na S4 simulant, waste loadings on dry basis of 14% to 15% have been achieved (Table 2.11).

Table 2.11. Solid Waste Loadings in DuraLith Waste Forms

	HSW[(a)]		SBW[(a)]	Waste Simulant[(b)]	HSW S1 Simulant[(c)]		HSW S4 Simulant[(c)]	
Waste Form Properties	TB9-4	TB9-1R	ED-SA3	Batch 1&2	S1-6X1R FS	S1-6X2R MK	S4-6X1 FS	S4-6X2 MK
Waste Loading (% wt)	2.63	5.75	9.00	2.70	7.39	7.60	14.16	15.26
Na Conc. (M)	2	~4	~1.9[(d)]	2	6	6	6	6

(a) Gong et al. (2006).
(b) Pierce et al. (2010b).
(c) Gong et al. (2011).
(d) The acidic waste was neutralized by using CaO and/or OPC (ordinary Portland cement) in addition to KOH.

2.3.3 Potential Adverse Impact Waste Constituents

There are a number of waste constituents that may adversely impact the performance of the waste form. The waste contains potentially leachable RCRA metals, such as Ag, As, Cr, Hg, and Pb. Therefore, the DuraLith should be capable of sequestering these contaminants and limiting their leaching. To achieve the highest possible waste loading, the waste may have to be concentrated through evaporation. Waste concentration results increased Na and nitrate molarities (increased ionic strength), which may adversely affect the mixing of the waste form and its setting properties, and also engender leaching of Na, The IDF Waste Acceptance Criteria (see Section 1.1.1) specifies that the leaching index for Na should be greater than 6.0.

DuraLith formulation also involves separate activation of the concentrated liquid waste before it is added to the dry ingredient mix. The activation process consists of adding fumed silica and other additives to the concentrated liquid waste. Because fumed silica typically contains minor amounts of silicon and/or silicon carbide when mixed with highly alkaline waste, these components produce hydrogen gas[1]. Therefore, the process has to be designed so that the gas evolution does not exceed the flammability limit. Also, if any additional gas evolution occurs upon mixing the activator solution with the dry ingredients, the resulting DuraLith monoliths may be more porous, thus engendering enhanced leachability of contaminants of concern (COCs). The leaching of COCs (such as Tc, I, Ag, As, Cd, Cr, Cu, Pb, and Sn) may depend on the number, size and distribution and interconnectivity of these trapped bubbles. However, if the waste form is demonstrated to meet the waste acceptance criteria, then gas bubble trapping is not an issue.

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[1] Recent unpublished work indicates that hydrogen evolution can be mitigated by substituting potassium silicate hydrate or calcined silica fume. Ian L. Pegg, VSL-CUA Personal Communication, April 19, 2011.

3.0 Waste Form Process Description

Preparing DuraLith geopolymer waste forms requires preprocessing the liquid waste before it is mixed into a dry ingredient blend. This section includes a description of the ingredients, additives, the process steps, processing times, temperatures, and curing times.

3.1 DuraLith Waste Form Ingredients

Based on the optimized formulation, a list of ingredients for making DuraLith waste forms has been suggested by Gong et al. (2011). These ingredients, their functions, and suggested sources are listed in Table 3.1. The main ingredients that constitute ~95% of the dry mass consist of blast furnace slag (36.5%), fine river sand (24.8%), metakaolin (14.7%), fumed silica (10.7%), and KOH (~8.0%). The remaining mass of the dry ingredients (~5%) constitutes the additives, such as copper slag (2.6%), NaOH (1.1%), ground zeolite type 5A (0.65%), ground IONEX Ag 900 (0.65%), and tin fluoride (0.31%). Chemical analyses of all these ingredients, except the caustics (KOH and NaOH), Type 5A ground Zeolite, and tin fluoride are listed in Table 2.4 and Table 2.5 in Section 2.0.

Table 3.1. DuraLith Formulation—List of Ingredients, Function and Suggested Sources

Ingredient	Function	Suggested Sources
Main Ingredients		
Ground blast furnace slag	Reactive binder	Lafarge North America
Fine River sand	Filler material	Local Sources
Metakaolin	Reactive binder	Thiele Kaolin Company
Fumed silica	Waste Activator	Norchem Corporation
Potassium hydroxide (KOH)	Activating Alkali	NOAH Technologies
Additives		
Ground copper slag	I sequestor	Opta Minerals
Sodium hydroxide (NaOH)	Activating Alkali	NOAH Technologies
IONEX Ag 900	I sequestor	Molecular Products
Zeolite Type 5A	Nucleator	--
Tin (II) Fluoride (SnF_2)	Tc Reductant	Alfa Aesar

The chemical analysis (Table 2.4 and Table 2.5) shows that these DuraLith ingredients are also a source of RCRA metals in the resulting waste form. The RCRA metal sources from the ingredients are listed in Table 3.2. Almost all the silver and tin in the waste form originates from the additives. Almost one half of the Cd and Pb in the waste form originates from four of the principal ingredients, namely metakaolin, sand, blast furnace slag, and fumed silica. Metakaolin is the principal source of Cr, accounting for almost three quarters of the total Cr found in the waste form.

Table 3.2. Significant RCRA Metal Sources in DuraLith Ingredients

RCRA Metal	Source Ingredient
Ag	Ground IONEX Ag 900
Cd	Metakaolin, Sand, Blast furnace slag, Fumed silica
Cr	Fumed silica, Sand, Blast furnace slag
Pb	Fumed silica, metakaolin, sand, blast furnace slag
Sn	Tin fluoride.

3.2 Process Steps

The DuraLith process steps outlined below are recommended by VSL/CUA (The Catholic University of America) (Gong et al. 2011) for casting 55-gallon size monoliths. All dry ingredients, if necessary, should be ground past a 200-mesh screen. The moisture content of the sand should be between 2.5 and 3.5 wt%.

3.2.1 Activator Solution Preparation

3.2.1.1 Ingredient List

- HSW waste (if S1 type concentrated to 6 M Na): 131.58 kg
- Tin fluoride: 1.28 kg
- KOH: 32.95 kg
- NaOH: 4.48 kg
- Silica Fume: 39.05 kg.

3.2.1.2 Process

1. Weigh the prescribed HSW mass.
2. Add tin fluoride to the HSW under stirring and keep stirring for at least 2 hours.
3. Continue stirring and slowly add the solid caustics (KOH and NaOH) to the waste solution; keep the temperature below 60°C with continual stirring.
4. Pour silica fume into the alkaline solution while stirring.
5. Weigh the total mass of the activator solution after all the silica fume has been added. Continue stirring for at least 24 hours.
6. At the end of 24 hours stirring, the activator solution should be thin and have little or no solid material on the bottom or on the edges of the container.
7. Weigh the mass of the activator solution again before preparing the 55-gal sample. Compensate water loss by adding tap water if the weight loss is more than 0.2%.

The mass of the activator is about 210 kg.

3.2.2 Composite Binder Preparation

3.2.2.1 Ingredient List

- Ground blast furnace slag: 150.74 kg
- Metakaolin: 60.85 kg
- River sand: 102.554 kg
- Type 5A ground zeolite: 2.70 kg
- Ground IONEX Ag: 2.70 kg
- Copper Slag: 10.8 kg
- Silica Fume: 5.40 kg.

3.2.2.2 Process

1. Dry mix ground blast furnace slag, metakaolin, fine river sand, IONEX Ag 900, zeolite type 5A, and copper slag until a homogeneous mixture is obtained.
2. Pour the activator solution into the mixer. Keep mixing for about 3 minutes or until a homogeneous paste has formed.
3. Immediately add the silica fume filler and mix for another 2 minutes. Longer mixing is not recommended as the temperature may rise, which may shorten the time available for pouring. Mixing should be completed with 10 minutes.
4. Pour the DuraLith paste into the storage container. This process should be completed within 30 minutes. Do not cover.
5. Clean mixer immediately.

3.3 Critical Process Parameters

The critical process parameters for DuraLith preparation are listed below.

3.3.1 Activator Solution Mixing

Once the activator solution preparation begins, the mixing has to be continuous until the activator solution is mixed with the dry ingredient. There will be sufficient mixing to make sure that all of the ingredients completely dissolve and also to prevent any undissolved solids in the activator from settling.

3.3.2 Mixing Time

In the DuraLith process, the activator solution has to be continuously mixed for ~24 hours to make certain that the silica fume dissolves to the fullest extent possible and that the solution cools. Once the activator solution is mixed with the binders, there will be a mixing time of 3 minutes or until a homogeneous mix is obtained. After the silica fume filler is added, an additional 2 minutes of mixing is recommended. The maximum mixing time allowed is 10 minutes with the casting of the monolith to be completed within 30 minutes. Therefore, the working time window between when the mixing is completed to finish the pouring is ~20 minutes. Recent unpublished work indicated that the working time window can be extended to 30 minutes by substituting 75% of the binder components (BFS and MK) with Class F fly ash.[1] If the mixing time is exceeded, the onset of the polymeric reactions may prevent free pouring of the DuraLith mixture. Similarly, if the casting is not completed within ~20 minutes, the resulting monolith may turn out to be more porous.

3.3.3 Hydrogen Evolution from Activator Solution

The activator solution preparation in the DuraLith process involves dissolving the silica fume in highly alkaline solution. The silica fume typically contains minor quantities of elemental silicon (0.2% to 0.6%) and silicon carbide (0.3% to 0.5%). The reaction of these minor components with the alkalis during the silica fume dissolution process results in the evolution of gaseous hydrogen (Zhang et al. 2000). The following set of reactions occurs when elemental silicon reacts with alkaline solution. The overall products of these reactions are the silicate ion and gaseous hydrogen (Equation 3.1). According to this reaction scheme, the reaction of each mole of elemental silicon with alkali (hydroxyl ion) results in the evolution of two moles of gaseous hydrogen and a mole of silicate ion. The results of the gas evolution studies conducted by Zhang et al. (2000) are shown in Figure 3.1. The data show a linear relationship for the average volume of gas produced (from the dissolution of silica fume) as a function of its elemental silicon content. According to the studies by Zhang et al. (2000), hydrogen constitutes ~80 to 96% of the total gas produced.

$$\begin{array}{l}
\mathrm{Si} \rightarrow \mathrm{Si}^{4+} + 4\,e^{-} \\
\mathrm{Si}^{4+} + 4\,\mathrm{H_2O} \rightarrow \mathrm{SiO(OH)_3^{-}} + 5\,\mathrm{H}^{+} \\
4\mathrm{H}^{+} + 4\,e^{-} \rightarrow 2\,\mathrm{H_2}\uparrow \\
\mathrm{H}^{+} + \mathrm{OH}^{-} \rightarrow \mathrm{H_2O} \\
\hline
\mathrm{Si} + 3\mathrm{H_2O} + \mathrm{OH}^{-} \rightarrow \mathrm{SiO(OH)_3^{-}} + 2\,\mathrm{H_2}\uparrow
\end{array} \qquad (3.1)$$

Therefore, depending on the elemental silicon content of the silica fume that may be used in preparing the activator solution, the hydrogen gas produced during silica fume dissolution in a full-scale DuraLith process needs to be vented so as not to exceed the flammability limit.

The issue of generation of hydrogen when using silica fume in the activator solution is a recent observation. There are other sources of silica such as potassium silicate hydrate (Kasolov from PQ Inc.) or calcined fumed silica that could be used in the preparation of the activator solution that do not have the residual silicon and therefore could be used to mitigate the hydrogen generation issue. Test data for secondary waste forms using these sources of silica are not available.

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[1] Ian L. Pegg, VSL-CUA, Personal Communication, April 19, 2011.

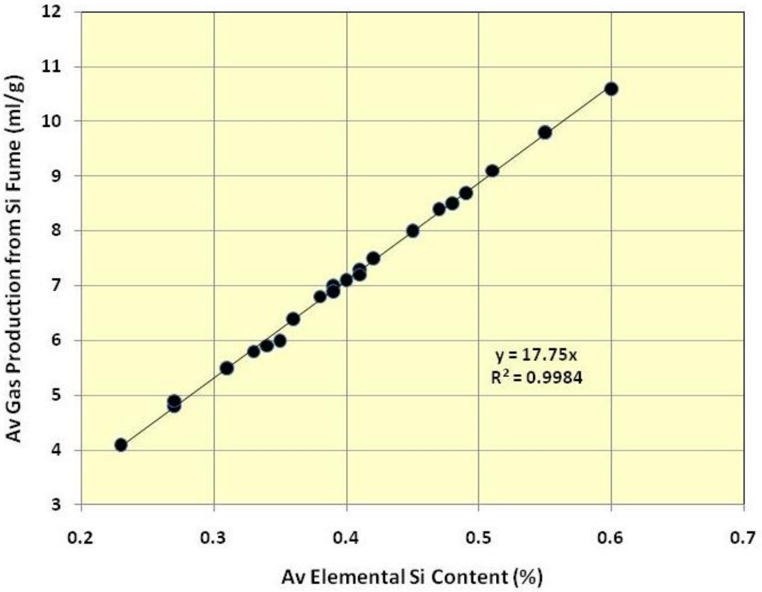

Figure 3.1. Gas Production from Silica Fume Dissolution as a Function of its Elemental Si Content

4.0 Waste Form Production Description

Based on the studies conducted at the VSL/CUA, a flow sheet for full-scale processing of HSW has been proposed by Gong et al. (2006). The following sections provide a description of the flowsheet, proposed equipment sizing, process control, off-gas treatment systems, and effluents resulting from the DuraLith process.

4.1 Process Description

The DuraLith process (Figure 4.1) is designed to receive the HSW continuously, process it, and generate monoliths and treat the resulting liquid, solid, and gaseous effluents. Lag storage tanks for HSW are recommended so that the DuraLith facility is decoupled from WTP operations. The waste (liquid and suspended solids if any) will then be transferred to the DuraLith process tank. The alkaline waste can be processed through an evaporator to concentrate and to achieve higher waste loading, thus reducing the capital cost of the facility and also decreasing the number of monoliths to be produced. If a waste concentration process is used, the condensate generated from the evaporator overheads would need treatment. Although the evaporator was not sized as part of this flowsheet, Gong et al. (2006) expect that the condensate will be generated at a rate of 2 to 3 gallons per minute. The condensate is expected to be low concentrations of radioactive constituents that can be treated by the existing onsite liquid effluent treatment facilities.

The first step in the process ((Figure 4.1) is to transfer the waste to the mixing tanks. For treating the HSW, the mixing tanks are designed to operate in parallel so that the feed process can be operated as a continuous batch process. The mixing tanks are initially fed with concentrated HSW, and chemical enhancers, such as tin fluoride and silver mordenite, are mixed in followed by solid caustic (KOH and NaOH) addition. This is immediately followed by adding silica fume, and it is mixed thoroughly to produce a homogenous activator solution. The mixing tanks are equipped with cooling coils to control the heat generated from the exothermic reaction. The activator solution will be mixed continuously for 24 hours to make sure that the silica fume completely dissolves before the process of alkali activationbegins.

The blended dry ingredients, consisting of BFS, metakaolin, sand, copper slag, Type 5 zeolite, IONEX Ag 900, and the filler silica fume, are stored in a supply hopper. The alkali activation process is initiated by pumping small batches of fully mixed activator solution and mixing with the appropriate quantities of dry blend in a ribbon blender. Blending is conducted until a fluid pourable DuraLith paste has formed. The total blending time should not exceed 10 minutes. The mixture is discharged from the ribbon blender to steel molds. Because the DuraLith paste sets up quickly (10 to 15 min)[1], each ribbon blender is sized to fill only one steel mold at a time. The molds are vibrated to achieve a uniform fill and to remove any gaps and air pockets that may occur during the fill operation. Once the ribbon blender is empty, it is immediately filled with another batch of activator solution from the mix tank to prevent any residual paste from the previous batch from hardening in the ribbon blender. Although the flowsheet depicts just one ribbon blender, three ribbon blenders are recommended to provide needed operational flexibility.

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[1] Recent unpublished data indicates that the setting time can be extended up to 30 minutes by using substituting 75% of the BFS and MK with Class F fly ash. Ian L. Pegg, VSL-CUA, Personal Communication, April 19, 2011.

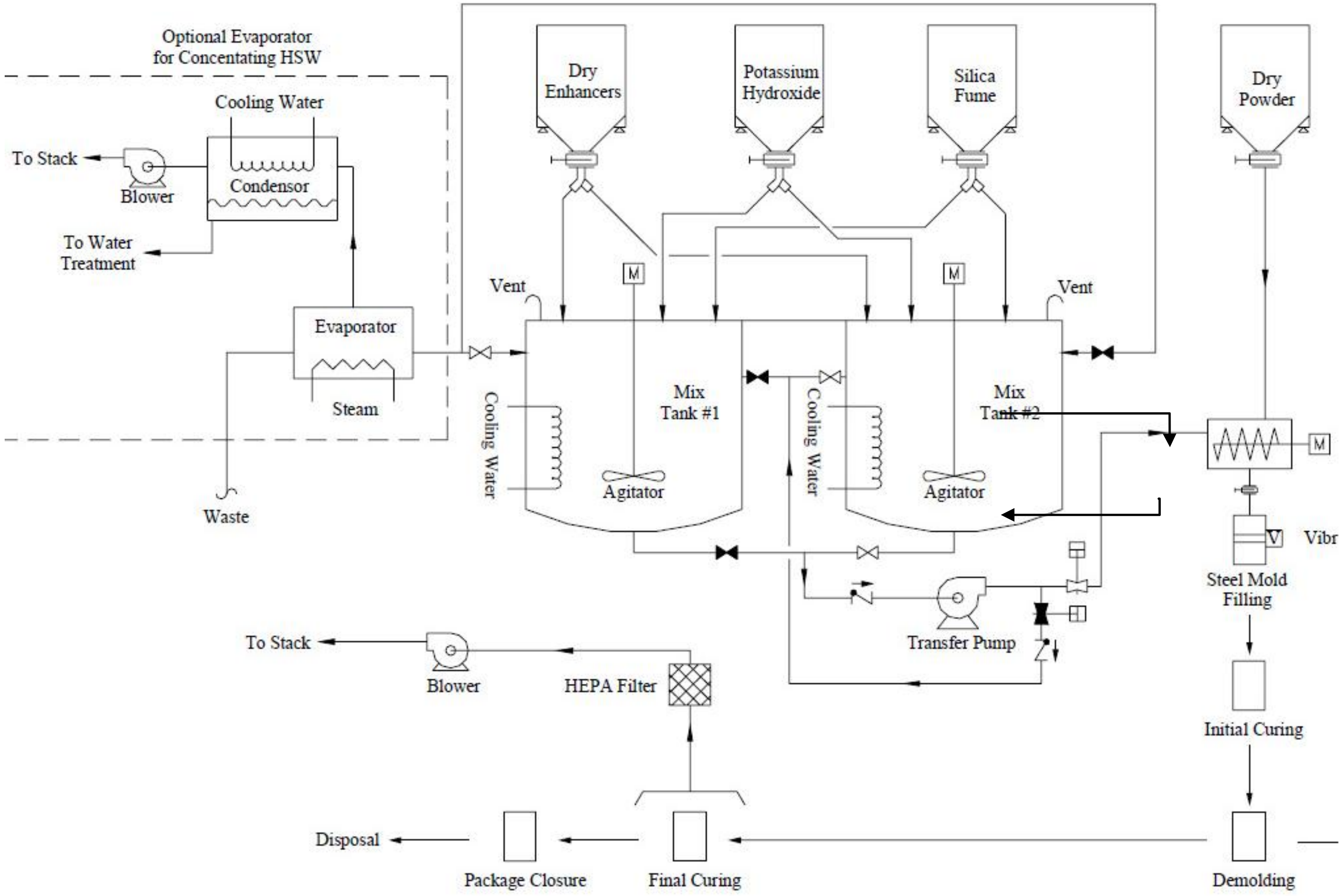

Figure 4.1. Hanford Secondary Waste Processing Flow Sheet (Gong et al. 2006)

The suggested steel molds are commercially available square containers, each with a capacity of about 48 cubic feet (1.75 cubic yards) of the freshly blended DuraLith paste. The steel molds will be lined with reinforced fabric bags manufactured from a geotextile or a similar fabric that will effectively contain the poured DuraLith paste and at the same time allow moisture to escape during the drying process. Lifting reinforced holes will be sewn into these liner bags to facilitate removal from the molds following a short setup period. The bags will then be stored in a well-ventilated drying area.

Following drying, the bags will be closed and prepared for final disposal. Due to the durability of the final product, it is anticipated that if DuraLith monoliths meet the waste acceptance criteria, they can be directly disposed of without the need for an overpack container.

4.2 Equipment Sizing and Description

Sizing of the major equipment and components for operating the DuraLith process has been provided as part of a previous study (Gong et al. 2006). The preliminary sizing and processing information compiled by these investigators is listed in Table 4.1. Because of low radiation levels of HSW, no shielding of the process equipment is included in the design. Following is a description and the design details for the major equipment in the DuraLith plant.

4.2.1 Waste Mixing Tanks

The mixing tanks for the activator solution will be equipped with continuous duty agitators and baffles that will provide high shear flow for thorough blending of activators and silica fume. These tanks are provided with vents to prevent pressure buildup during filling access ports for adding activators and silica fume. A set of cooling coils will be used to control the temperature of the solution that will heat up due to exothermic reaction. The temperature is controlled at a level to enhance the rate of dissolution of the silica fume. Hydrogen generation mitigation will be needed if silica fume is used as a silica source for the activator solution.

4.2.2 Dry Chemical Silo

The enhancers and solid potassium and sodium hydroxides and silica fumes will be stored in separate appropriately designed silos. These silos will be equipped with load cells to monitor the accuracy of chemical additions into the mixing tank, and conveyor systems will be used to transfer the chemicals. Knife gate valves will be used to isolate the chemicals from the conveying equipment. The storage and conveyance of solid alkalis (potassium hydroxide and sodium hydroxide) will be conducted with due attention to their corrosivity and hygroscopic nature. The capacity of each silo will be sufficient to operate the DuraLith plant for at least a week. Multiple silos will be deployed so that one set of silos could be loaded while the second set is in use. The silos were designed so that the height of the cylindrical portion was 3× to 4× times the diameter.

Table 4.1. Basic Design Parameters for DuraLith Plant Equipment

Parameter	HSW (Non-concentrated)	HSW (Concentrated)
Design Assumptions		
Average Waste Receipt Rate	4.8 gpm (800,000 L/month)	4.8 gpm (800,000 L/month)
Assumed Plant Availability	80%	80%
Processing Duration	17 yrs	17 yrs
Design Waste Feed Rate (incorporates availability)	6.0 gpm	2.8 gpm (after evaporation)
Batch Cycle Time	1 day	1 day
Mix Tank Basic Design		
Batch Volume	8700 gal	4000 gal
Tank Diameter	12 ft	8.5 ft
Tank Height	15 ft	10 ft
Number of Tanks	2	2
Dry Enhancer Silo		
Batch Weight	145 lb	77 lb
# of Batches Contained in Silo	20	20
Volume of Silo	42 ft^3	22 ft^3
Silo Diameter	2.5 ft	2 ft
Silo Height*	10 ft	8.5 ft
# of Silos Required	2	2
Potassium and Sodium Hydroxide Silo		
Batch Weight	39,700 lb	11,600 lb
# of Batches Contained in Silo	5	5
Volume of Silo	5,170 ft^3	1,510 ft^3
Silo Diameter	12 ft	8 ft
Silo Height*	54 ft	36 ft
# of Silos Required	2	2
Silica Fume Silo		
Batch Weight	31,400 lb	12,600 lb
# of Batches Contained in Silo	5	5
Volume of Silo	6,800 ft^3	2,730 ft^3
Silo Diameter	13 ft	10 ft
Silo Height*	60 ft	42 ft
# of Silos Required	2	2
Dry Chemical Silo		
Batch Weight	166,200 lb	30,100 lb
# of Batches Contained in Silo	5	5
Volume of Silo	43,200 ft^3	7,820 ft^3
Silo Diameter	25 ft	14 ft
Silo Height*	106 ft	61 ft
# of Silos Required	2	2
Blender System		
Blender Volume	48 ft^3 (360 gal)	48 ft^3 (360 gal)
# of Blenders Required	3	2
Final Waste Form		
Waste Form Size	4 ft × 4 ft × 3 ft	4 ft × 4 ft × 3 ft
Daily Production Rate	22	10
Total Number Produced over Lifetime	~134,000	~62,000

Source: Gong et al. (2006).

4.2.3 Ribbon Blenders

The solid ingredients will be blended with the activator solution to produce the DuraLith product paste by using a double ribbon blender system. The activator solution will be transferred via pumps while the solid ingredients will be conveyed from the appropriate silos in to the blender. Upon completion of the blending, the DuraLith paste will be dispensed through a valve into lined steel molds. The capacity of each blender is sufficient to completely fill a single steel container. To prevent any buildup of the DuraLith paste in the ribbon blenders, the activator solution from the mixing tank will be continuously circulated through the blenders until a fresh batch of paste is needed to be mixed by adding dry ingredients.

4.2.4 Final Waste Form Product

The DuraLith monolith contained in geotextile bags within steel drum molds will be lifted out and transported to a well-ventilated storage space to complete curing/drying for several weeks at room temperature.

4.3 Existing Facilities and Cost Data

Currently, there are no pilot-scale or full-scale DuraLith plants either under construction or in operation. Therefore, operational costs for producing DuraLith monoliths using HSW are unavailable.

5.0 Waste Form Physical Properties

For DuraLith Waste forms, only limited data are available for the heat of hydration and the heat generated during polymeric reactions. Thermal conductivity measurements or porosity determinations have not been made for this waste form.

5.1 Heat of Hydration and Reaction

Heat is generated when the activator solution is prepared. The heat evolution is from the alkali dissolution of silica fume, which is an exothermic reaction. Gong et al. (2011) conducted a study of heat evolution, and the data they generated are shown in Figure 5.1. The temperature measurement shown was measured while preparing a ~7-kg batch of activator solution. The data show that the initial addition of the alkalis (KOH and NaOH) engenders an exothermic reaction that raises the temperature of the mix to ~45°C. Small incremental additions of alkali with mixing were continued over a period of 5 hours to maintain the temperature at ~45°C. Next, all the silica fume was added within the next 10 minutes and that resulted in a slight drop in temperature because of the ambient temperature of the mass of silica fume. As the alkali dissolution of silica fume proceeded, the exothermic reaction raised the temperature to a peak at ~67°C at 9 hours since the activation was initiated.

As the mixing was continued, the temperature dropped smoothly, and at the end of ~24 hours, the temperature of the activator solution began to stabilize at ~27°C.

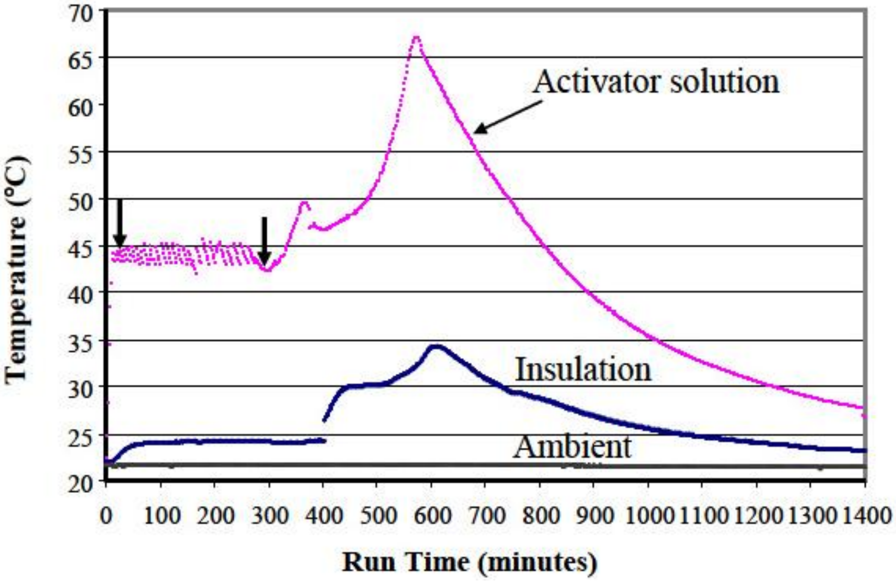

Figure 5.1. Temperature Profile During Activator Solution Preparation. The first vertical arrow on the left indicates the beginning of alkali addition. The second vertical arrow on the left indicates the beginning of Silica fume addition (Gong et al. 2011).

Heat generation also occurs after the activator solution is blended into dry ingredients to make DuraLith paste. The alkali activation and subsequent polymerization reactions involving aluminosilicate ingredients are exothermic in nature and raise the temperature of the reacting paste. The temperature profiles during the initial reaction and the curing of 5-gallon batches of blast furnace slag-based and metakaolin-based DuraLith pastes are shown in Figure 5.2 and Figure 5.3.

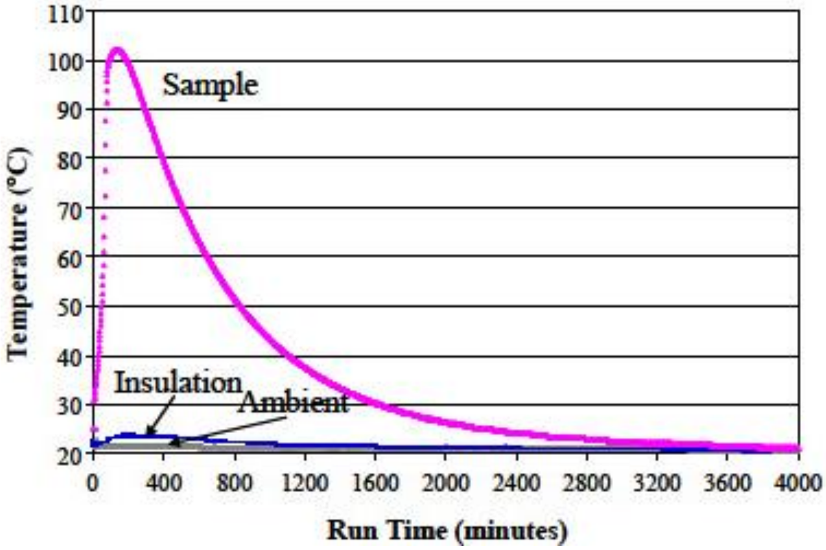

Figure 5.2. Temperature Profile for a 5-Gallon Batch of Blast Furnace, Slag-Based DuraLith Paste (Gong et al. 2011)

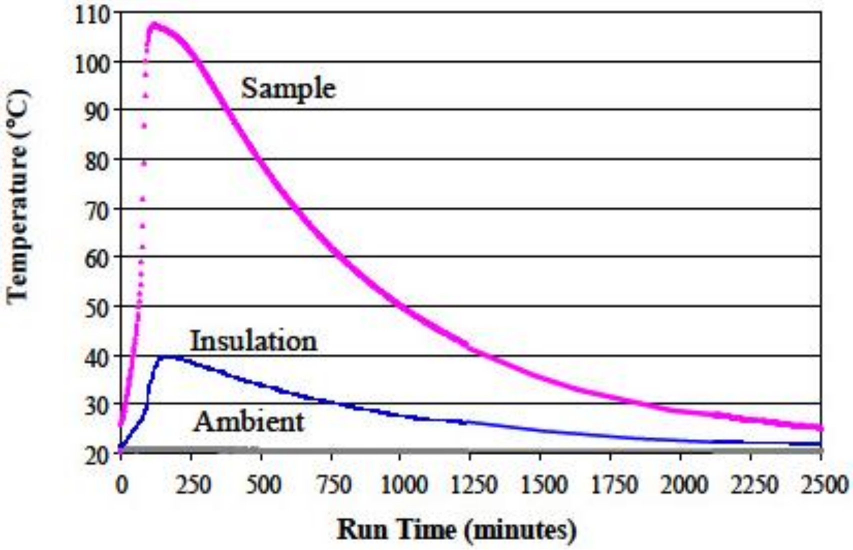

Figure 5.3. Temperature Profile for a 5-Gallon Batch of Metakaolin-Based, DuraLith Paste (Gong et al. 2011)

The data showed that the polymerization reaction generates intense heat with a concomitant rapid rise in temperature (Figure 5.2 and Figure 5.3). The temperature in both pastes reached a peak of ~107°C within 2 hours. As the kinetically rapid part of the polymerization reaction is completed, there is a smooth drop in temperature during the following slower curing reaction phase.

Heat evolution during alkali activation of aluminosilicate materials has been studied extensively (Harbour et al. 2007, Harbour and Edwards 2008, 2009; Granizo et al. 2000; Buchwald et al. 2009; Kumar et al. 2010). Typically, the heat evolution during the polymerization reaction depends on factors such as the material being activated, the alkali concentration in the waste, and the solid-to-solution ratio. Typical heat evolution measurements for alkali activated polymeric reactions at the peak (50 to 70 hrs) are listed in Table 5.1.

Table 5.1. Heat Evolution from Alkali-Activated Geopolymeric Reaction

Activated Binder	Waste Type	Heat Generated (J/g)	Reference
Metakaolin	12 M NaOH 15 M NaOH 18 M NaOH	232 – 469 314 – 602 399 - 648	Granizo et al. 2000
Blast furnace slag	Solvent extr. waste	250	Harbour et al. 2007, 2008, 2009
Salt stone (10% OPC + 45%BFS + 45% fly ash)	Solvent extr. waste	120	Harbour et al. 2007, 2008, 2009
Class F fly ash	Solvent extr. waste	7	Harbour et al. 2007, 2008, 2009
Blast Furnace slag	~4 M NaOH	~100	Buchwald et al. 2009
Blast Furnace slag	~8 M NaOH	~150	Buchwald et al. 2009
Metakaolin	~4 M NaOH	~180	Buchwald et al. 2009
Metakaolin	~8 M NaOH	~250	Buchwald et al. 2009
Metakaolin 25% + Blast Furnace Slag 75%	~4 M NaOH	~140	Buchwald et al. 2009
Metakaolin 25% + Blast Furnace Slag 75%	~8 M NaOH	~180	Buchwald et al. 2009
Metakaolin 50% + Blast Furnace Slag 50%	~4 M NaOH	~90	Buchwald et al. 2009
Metakaolin 50% + Blast Furnace Slag 50%	~8 M NaOH	~180	Buchwald et al. 2009
Blast Furnace Slag	6 M NaOH	135	Kumar et al. 2010
Class F Fly Ash	6 M NaOH	15	Kumar et al. 2010

The data indicate that the heat evolution depends on the nature of the binder and the alkali concentration. Typically, metakaolin generates more heat than blast furnace slag when activated with equimolar alkali concentrations.

5.2 Density

Density measurements were conducted by Russell et al. (2006) on DuraLith specimens prepared with HSW and SBW by Gong et al. (2006). The average density of HSW-containing DuraLith specimens was 1.76 g /cm^3, whereas the average density of SBW-containing specimens was measured to be 1.86 g/cm^3. DuraLith samples based on BFS containing 6M Na simulant (S1) have densities of about 2.0 g/cm^3.[1]

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[1] Ian L. Pegg, VSL-CUA Personal Communication. 4-19-2011.

6.0 Waste Form Performance

6.1 Leach Tests

The leaching tests are conducted on waste forms to evaluate its short- and long-term performance in the disposal environment. There are two categories of leaching tests. The first category of tests is the regulatory tests. These are standard tests that are conducted to assess whether a waste form meets the regulatory requirements in terms of contaminant diffusivity and leachability. The ANSI/ANS-16.1 and the EPA TCLP tests belong to the category of regulatory leach tests. The second category of tests is designed to:

- Assess short- and long-term leaching performance
- Generate data to determine the dominant release mechanism (reactions and kinetics) for each COC
- Provide a database for modeling and predicting the contaminant release from the waste forms over the life-span of a repository that may extend over thousands of years.

The long-term performance of various waste forms has been assessed by using data from a number of test methods. These are the Product Consistency Test (PCT), Single Pass Flow Through (SPFT) test, Pressurized Unsaturated flow (PUF) test, Vapor Hydration Test (VHT), and, more recently, three proposed EPA draft methods (EPA 2009a, Method 1313; EPA 2009c 1315, and EPA 2009b, Method 1316). If approved, these draft methods would replace the regulatory-based TCLP test (EPA 2000, Method 1311).

The non-regulatory PCT and the EPA draft methods 1313 and 1316 have been used to assess the release of COCs from DuraLith waste forms. Following is a brief description of these methods and the results obtained. The description of regulatory tests and the results for DuraLith are discussed in the next section (Section 7, Waste Acceptance Criteria). The detailed of analytical methods used for the leachate analyses can be obtained from appropriate references from which the results have been collected.

6.1.1 EPA 1315 Leach Test

The draft EPA Method 1315 (EPA 2009c) is a dynamic leach experiment that consists of submerging a monolithic sample in deionized water (DIW) at a fixed liquid, volume-to-solid, surface-area ratio. The sampling was done at fixed periods of time as cumulative leaching times 0.08, 1, 2, 7, 14, 28, 42, 49, and 63 days (EPA 2009c). At each sampling interval, the leaching fluid is removed and replaced with fresh fluid. A schematic of this process is shown in Figure 6.1.

The geometric surface area is used in this test method and calculated based on the cylindrical dimensions of the sample. At each of the nine pre-determined leaching intervals, the sample mass is recorded, and the leaching solution is changed. This method is similar to ANSI/ANS 16.1 (ANSI 1986), but the leaching intervals are modified, and the process of mass transfer can be interpreted by more complex release models that account for physical retention of the porous medium and chemical retention at the pore wall through geochemical speciation modeling.

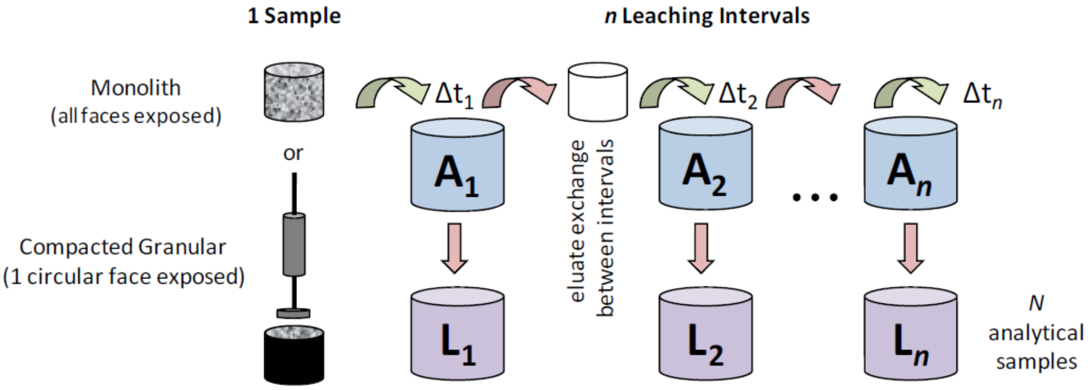

Figure 6.1. EPA 1315 Testing Scheme

In this test, a cylindrical monolith sample (2-inch diameter by 4-inch height) is placed into the center of a leaching vessel and mixed with DIW to maintain a solid-to-solution ratio of 9 ±1 mL of leachant per cm^2 of sample. The sample stand and holder are used to maximize the contact area of the sample with the leaching solution. In between the sampling/replacement intervals, the experimental vessels are covered with a lid. The solution exchanges are made at leaching times of 2 hours and 1, 2, 7, 14, 28, 42, 49, and 63 days. Leachate samples collected during these intervals are used to measure pH, electrical conductivity, and redox potential. Chemical analyses of the leachates are conducted following filtration using a 0.45-µm syringe filter.

The observed diffusivity for each constituent was calculated using the analytical solution, Equation 6.1, for simple radial diffusion from a cylinder into an infinite bath as presented by Crank (1986).

$$D_i = \left[\frac{M_{ti}}{2\rho C_0\left(\sqrt{t_i} - \sqrt{t_{i-1}}\right)}\right]^2 \tag{6.1}$$

where D_i = observed diffusivity of a specific constituent for leaching interval, *i* [m^2/s]
M_{ti} = mass released during leaching interval *i* [mg/m^2]
t_i = cumulative contact time after leaching interval, *i* [s]
t_{i-1} = cumulative contact time after leaching interval, *i-1* [s]
C_o = initial leachable content [mg/Kg]
ρ sample density [kg-dry/m^3].

The mean observed diffusivity for each constituent can be determined by taking the average of the interval observed diffusivity with the standard deviation.

The LI, the parameter derived directly from immersion test results evaluates diffusion-controlled contaminant release with respect to time. The LI is used as a criterion to assess whether solidified/stabilized waste will likely be acceptable for subsurface disposal in waste repositories. In most cases, the solidified waste is considered effectively treated when the LI value is equal to or greater than 9. The LI is calculated with Equation (6.2)

$$LI_n = -\log\left[\frac{D_n}{cm^2/s}\right] \tag{6.2}$$

where *LI* is the leach index, and D_n is the effective diffusivity for elements of interest (cm^2/s) during the leach interval *n*.

The results of the EPA 1315 leach tests on two of the DuraLith waste forms are tabulated in (Table 6.1). The data show that ^{99}Tc, Ag, and Hg have very low diffusivities with a range of LI values of ~8 to 11, 16 to 17, and 10 to 11, respectively. The LI value for Na ranged from ~8 to 9, whereas I showed the highest diffusivity with LI values ranging from 4 to 8. The target LI for Tc, Na, and I are >9, >6, and >11 respectively. These targets need to be validated and verified based on more recent and future IDF performance assessments.

6.1.2 Product Consistency Test

The PCT was conducted on the DuraLith samples containing HSW (Russell et al. 2006).[1] To conduct this test, the DuraLith waste form was ground and sieved, and 0.84 to 2.00 mm and 75- and 150-µm particle fractions were retained for testing. Approximately 1.5 g of ground waste form was weighed and placed into a 22-mL desensitized Type 304L stainless steel container (Figure 6.2). The volume of de-ionized water for each sample was measured by mass and added to the requisite stainless steel container. The waste form was precisely weighed and the leachate volume precisely controlled to achieve a solution volume-to-waste form ratio of 10 mL/g waste form. The container and its contents were held without agitation at 90°C for 1 day (-10 to +20 mesh particle size) and 7 days (-100 to +200 mesh particle size).

The normalized release was calculated using the following Equation (6.3):

$$NL_i = \frac{c_i}{f_i(\frac{SA}{V})} \tag{6.3}$$

where NL_i = normalized release, g/m^2
c_i = concentration of ith element in the solution, g_i/L
f_i = fraction of ith element in the unleached waste form (unitless)
SA/V = surface area of the final waste form divided by the leachate volume, m^2/L.

At the end of tests, all DuraLith samples had final pH values of ~12.00. Among all monitored constituents, Na and K showed the highest normalized releases from the waste form. This is to be expected because DuraLith is alkali-activated geopolymer. The order of magnitude differences in the normalized release rates for the constituents from -100 to +200 mesh particles and the -10 to +20 Mesh particles is reflective of the relative surface areas of the ground DuraLith material. The surface area of finer mesh material was 2.972 m^2/L, whereas the surface area of the coarser material was 0.233 m^2/L.

6.1.3 EPA 1313 Leach Test

The EPA 1313 test method (EPA 2009a) has been used on DuraLith samples tested during the Phase I investigations of candidate secondary waste forms (Pierce et al. 2010b). The EPA Method 1313 (Liquid-Solid Partitioning as a Function of Extract pH) is a static test method where a set of parallel extraction

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[1] PCT data are not available for the new DuraLith formulations.

experiments are conducted in dilute acid or base laden DIW at a fixed pH (pH range from 4 to 12) and fixed liquid-to-solid ratio (10 mL/g) (EPA 2009a).

Table 6.1. Results of EPA 1315 Leach Test on DuraLith Samples (Pierce et al 2010b)

Cum Leach Time (Days)	pH	Na (cm^2/s)	LI_{Na}	Ag (cm^2/s)	LI_{Ag}	Hg (cm^2/s)	LI_{Hg}	I (cm^2/s)	LI_I	^{99}Tc (cm^2/s)	LI_{Tc}
DuraLith Batch #1											
0.08	10.74	1.50E-09	8.8	<2.17E-16	15.7	<8.07E-11	10.1	<4.75E-07	6.3	3.13E-11	10.5
0.08	10.75	2.10E-09	8.7	<2.16E-16	15.7	<8.03E-11	10.1	4.38E-05	4.4	1.72E-10	9.8
1	11.33	2.10E-09	8.7	<3.54E-17	16.5	<1.32E-11	10.9	4.71E-05	4.3	1.82E-11	10.7
1	11.39	2.90E-09	8.5	<3.52E-17	16.5	<1.31E-11	10.9	4.92E-05	4.3	3.61E-11	10.4
2	11.41	3.80E-09	8.4	<1.07E-16	16.0	1.08E-10	10.0	7.77E-06	5.1	3.88E-11	10.4
2	11.47	4.90E-09	8.3	<1.07E-16	16.0	1.29E-10	9.9	1.23E-05	4.9	4.95E-11	10.3
7	11.86	3.20E-09	8.5	<1.19E-17	16.9	<4.41E-12	11.4	6.79E-06	5.2	3.78E-11	10.4
7	11.94	4.50E-09	8.4	<1.18E-17	16.9	<4.38E-12	11.4	7.69E-06	5.1	8.22E-11	10.1
14	11.65	4.70E-09	8.3	<1.50E-17	16.8	<5.56E-12	11.3	<3.27E-08	7.5	1.89E-11	10.7
14	11.64	4.80E-09	8.3	<1.49E-17	16.8	2.98E-11	10.5	7.39E-08	7.1	5.23E-11	10.3
28	11.81	3.00E-09	8.5	<7.51E-18	17.1	<2.79E-12	11.6	6.83E-08	7.2	9.85E-12	11.0
28	11.56	2.80E-09	8.6	<7.46E-18	17.1	3.04E-11	10.5	<6.52E-08	7.2	2.68E-11	10.6
42	11.64	2.30E-09	8.6	<1.30E-17	16.9	<4.83E-12	11.3	<1.14E-07	6.9	7.74E-12	11.1
42	11.71	2.20E-09	8.7	<1.29E-17	16.9	<4.80E-12	11.3	<1.13E-07	7.0	1.48E-11	10.8
49	11.13	2.10E-09	8.7	<6.58E-17	16.2	<2.44E-11	10.6	<5.75E-07	6.2	7.21E-12	11.1
49	11.18	2.20E-09	8.7	<6.53E-17	16.2	5.32E-11	10.3	<5.71E-07	6.2	1.25E-11	10.9
63	11.42	1.40E-09	8.9	<2.09E-17	16.7	<7.77E-12	11.1	<1.83E-07	6.7	3.76E-12	11.4
63	11.44	1.40E-09	8.9	<2.08E-17	16.7	2.36E-11	10.6	<1.82E-07	6.7	8.87E-12	11.1
DuraLith Batch #2											
0.08	10.36	3.95E-09	8.4	<3.48E-16	15.5	<3.11E-11	10.5	3.94E-06	5.4	2.53E-09	8.6
0.08	10.59	4.79E-09	8.3	<3.90E-16	15.4	<3.49E-11	10.5	2.21E-06	5.7	3.58E-09	8.5
1	11.16	3.08E-09	8.5	<5.00E-17	16.3	<4.47E-12	11.3	2.38E-06	5.6	2.87E-09	8.5
1	11.15	3.73E-09	8.4	<5.61E-17	16.3	<5.01E-12	11.3	1.63E-05	4.8	4.27E-09	8.4
2	10.96	4.96E-09	8.3	<1.44E-16	15.8	<1.29E-11	10.9	5.09E-06	5.3	6.32E-09	8.2
2	10.92	5.70E-09	8.2	<1.61E-16	15.8	<1.44E-11	10.8	2.43E-05	4.6	9.93E-09	8.0
7	11.40	5.32E-09	8.3	<1.78E-17	16.7	1.64E-12	11.8	1.04E-05	5.0	1.22E-09	8.9
7	11.42	5.77E-09	8.2	<1.99E-17	16.7	1.94E-12	11.7	1.92E-05	4.7	1.82E-09	8.7
14	11.51	4.24E-09	8.4	<2.22E-17	16.7	<1.99E-12	11.7	4.70E-08	7.3	2.81E-11	10.6
14	11.50	5.48E-09	8.3	<2.49E-17	16.6	<2.23E-12	11.7	2.75E-07	6.6	3.58E-11	10.4
28	11.81	3.38E-09	8.5	<1.12E-17	16.9	<1.00E-12	12.0	<3.37E-08	7.5	2.28E-11	10.6
28	11.59	3.25E-09	8.5	<1.26E-17	16.9	<1.13E-12	11.9	<3.78E-08	7.4	2.22E-11	10.7
42	11.39	2.06E-09	8.7	<1.84E-17	16.7	<1.65E-12	11.8	<5.53E-08	7.3	1.83E-11	10.7
42	11.39	2.25E-09	8.7	<2.07E-17	16.7	<1.85E-12	11.7	<6.20E-08	7.2	2.02E-11	10.7
49	11.00	2.18E-09	8.7	<1.00E-16	16.0	<8.95E-12	11.0	<3.01E-07	6.5	2.87E-11	10.5
49	11.11	2.60E-09	8.6	<1.12E-16	15.9	<1.00E-11	11.0	<3.37E-07	6.5	3.21E-11	10.5
63	11.31	1.23E-09	8.9	<3.04E-17	16.5	<2.71E-12	11.6	<9.11E-08	7.0	2.66E-11	10.6
63	11.37	1.52E-09	8.8	<3.41E-17	16.5	<3.05E-12	11.5	<1.02E-07	7.0	2.18E-11	10.7

Figure 6.2. A Picture of Dissembled PCT Vessel (Russell et al. 2006)

The PCT results for DuraLith are tabulated in Table 6.2 and Table 6.3.

Table 6.2. PCT Data for DuraLith Samples[(a)]

Specimen #	Waste Type[(b)]	Initial pH	Final pH	Na	K	Si	Mg	Al	P
				g/m^2					
VSL/HSW TB-9R3-B-S-4	HSW[(b)]	5.57	12.11	17.74	8.91	0.656	<0.005	0.025	--
VSL/HSW TB-9R3-C-S-6	HSW[(b)]	5.57	12.21	17.53	8.69	0.450	<0.049	0.870	--
VSL/SBW ED-SA3-B-1	SBW[(c)]	5.57	11.93	20.43	18.23	0.117	<0.001	0.061	--
VSL/SBW ED-SA3-C-2	SBW[(c)]	5.57	11.99	20.33	23.86	0.137	<0.011	0.079	--

(a) 7-day test conducted with -100 to +200 Mesh particles.
(b) HSW = Hanford Secondary Waste.
(c) SBW = Idaho Sodium-bearing Waste. Ref: Russell et al. 2006

Table 6.3. PCT Data for DuraLith Samples[(a)]

Specimen #	Waste Type	Initial pH	Final pH	Na	K	Si	Mg	Al	P
				g/m^2					
VSL/HSW TB-9R3-B-S-4	HSW[(b)]	5.57	12.11	211	107	6.48	<0.061	0.138	--
VSL/HSW TB-9R3-C-S-6	HSW[(b)]	5.57	12.21	218	106	3.59	<0.010	0.587	--
VSL/SBW ED-SA3-B-1	SBW[(c)]	5.57	11.93	228	194	1.49	<0.001	0.994	--
VSL/SBW ED-SA3-C-2	SBW[(c)]	5.57	11.99	203	183	1.67	<0.011	1.520	--

(a) 1-day test conducted with -10 to +20 Mesh particles.
(b) HSW = Hanford Secondary Waste,
(c) SBW = Idaho Sodium-bearing Waste. Ref: Russell et al. 2006

Before initiating the static test, a series of pre-titrations were conducted at a fixed liquid-to-solid ratio (10 mL/g) using <0.3-mm sized material. After a 24-hour period of mixing in the absence of acid or base additions, the sample slurry was centrifuged, the supernatant was removed, and it was used to determine the equilibrated pH. Since the measured pH of the leachate solutions for the DuraLith was high (pH ~12 to 13), a pre-titration was developed based upon dilute HNO_3 additions to decrease the pH from 12 to lower targeted values after 24 hours of equilibration. Analytical grade HNO_3 (Optima) was used to prepare a solution of 2 N HNO_3 for these experiments.

Based upon the pre-titration results, test samples were prepared by mixing 10 g of <0.3-mm sized material with a predetermined amount of 2 N HNO_3 and bringing the samples to volume with DIW. All samples were placed on a platform shaker and allowed to mix at room temperature (23 ±2°C) for 24 hours. After mixing, the extractant vessels were centrifuged (minimum at 4000±100 RPM) for 10±2 minutes, and the decanted clear supernatant was filtered using a 0.45-µm polypropylene membrane syringe filter, collected in a vial with minimal head space, and submitted for chemical analysis.

The results of the EPA 1313 test are shown in Table 6.4. The data showed that the concentrations of Cd and Pb in the leachates at all pH values and Cr in the pH range of ~6 to 8 were below the detection limits. The leaching of Ag and ^{99}Tc were very low under all pH conditions whereas Hg showed slightly higher leaching at the highest pH. The leaching of I was relatively constant at all pH values with concentrations ranging from ~25 to 32 µg/L. The leachate concentrations of Ag, Cd, Cr, and Pb from both the DuraLith samples at all pH values were generally one to three orders of magnitude less than the UTS limits specified by EPA for land disposal of wastes.

Table 6.4. Results of the EPA 1313 Tests on DuraLith Samples

pH (SU)	EC (mS/cm)	Eh (mV)	$CaCO_3$ Alkalinity (mg/L)	Cd	Cr	Pb	Ag	Hg	^{99}Tc	I
							(µg/L)			
DuraLith Batch #1										
3.66	43.5	364	0	ND	101	ND	7.53	0.17	5.07	32.20
3.72	43.0	364	0	ND	164	ND	5.60	0.12	5.00	29.20
5.42	24.0	313	32	ND	ND	ND	2.74	2.69	6.68	28.10
5.94	23.8	306	68	ND	ND	ND	2.68	4.81	6.90	29.20
7.72	15.4	273	174	ND	1.7	ND	2.52	24.20	7.88	27.70
7.85	15.5	273	174	ND	ND	ND	2.38	27.60	7.98	28.30
12.20	6.9	137	1248	ND	39	ND	2.50	66.40	8.77	28.90
12.20	7.2	133	1302	ND	45	ND	2.79	68.90	9.32	29.90
DuraLith Batch #2										
3.79	38.1	251	0	ND	44	ND	5.18	0.22	3.77	28.90
4.04	38.4	352	0	ND	36	ND	4.68	0.18	3.70	28.50
6.41	21.7	301	129	ND	ND	ND	5.41	3.33	4.32	26.30
6.58	21.5	304	162	ND	ND	ND	6.57	3.60	4.37	26.50
8.25	13.9	270	204	ND	ND	ND	5.77	9.43	4.56	25.20
8.38	13.8	260	190	ND	ND	ND	6.37	9.65	4.65	25.70
12.00	6.3	138	1013	ND	59	ND	4.41	12.50	2.97	25.80
12.00	6.2	142	1067	ND	38	ND	5.74	14.00	2.95	27.10
Universal Treatment Standards 40 CFR 268.48 Subpart D				110	600	750	140	200	NS	NS

ND = Not detected; NS = Not specified; Reference – Pierce et al. (2010b).

6.1.4 EPA Method 1316 Leach Test

Similar to 1313, EPA Method 1316 (EPA 2009b) also is a static test method that uses DIW as the leachant instead of a dilute acid or base at a variety of liquid-to-solid ratios (EPA 2009b). The purpose of this test method is to evaluate the effect of differing liquid-to-solid ratios on the release of contaminants. These experiments were conducted by adding DIW to the test vessel containing a predetermined amount of powdered material (<0.3 mm). These experiments were conducted at three different liquid-to-solid ratios (10, 5, and 2 mL/g). After preparation, all the samples were placed on a platform shaker and allowed to mix for 24 hours. After the 24-hour contact time was complete, the slurry samples were centrifuged, and clear supernatants were filtered using a syringe filter (0.45-µm size polypropylene membrane). The filtrate was collected in vials with minimal head space and submitted for chemical analyses.

The results of the EPA 1316 test are listed in Table 6.5. One notable difference is that the Batch #2 DuraLith sample appears to leach significantly more Cd and Cr than the Batch #1 sample. Both samples also show higher concentrations of all contaminants in leachates generated at the lowest LS (2 mL/g) ratio. However, Ag, Cd, Cr, Hg, and Pb concentrations in the leachates are well below the UTS limits (Table 6.5).

Table 6.5. Results of the EPA 1316 Tests on DuraLith Samples

pH (SU)	LS Ratio (ml/g)	EC (mS/cm)	Eh (mV)	$CaCO_3$ Alkalinity (mg/L)	Cd	Cr	Pb	Ag	Hg	Tc	I
					(µg/L)						
DuraLith Batch #1											
12.20	10	6.9	137	1248	ND	39	ND	2.50	66.4	8.77	28.90
12.20	10	7.2	133	1302	ND	45	ND	2.79	68.9	9.32	29.90
12.40	5	11.1	104	1874	ND	3.7	ND	5.57	57.2	17.69	64.20
12.50	5	11.0	110	1854	ND	8.6	ND	9.31	55.7	17.86	62.90
12.60	2	20.9	93	3008	ND	10.0	ND	5.55	136.0	38.22	184.00
12.70	2	21.0	97	3102	ND	6.3	ND	5.91	125.0	35.30	184.00
DuraLith Batch #2											
12.00	10	6.3	138	1013	ND	59	ND	4.41	12.50	2.97	25.80
12.00	10	6.2	142	1067	ND	38	ND	5.74	14.0	2.95	27.10
12.00	5	9.2	113	1520	6.67	124	6.84	4.05	44.3	8.52	56.80
12.00	5	9.1	112	1446	5.64	118	1.40	3.64	41.8	8.41	54.60
12.10	2	16.9	92	2241	5.53	289	1.55	3.67	116.0	21.90	152.00
12.10	2	16.8	96	2175	3.89	275	1.64	3.59	113.0	19.20	160.00
Universal Treatment Standards 40 CFR 268.48 Subpart D					110	600	750	140	200	NS	NS

ND = Not detected; NS = Not specified; Reference – Pierce et al. (2010b).

6.2 Contaminant Speciation and Containment Mechanisms

Currently, no published data exist regarding the contaminant bonding, the redox speciation, and the phase associations of COCs in the DuraLith matrix. Currently, work is in progress to elucidate the speciation and containment mechanisms for Tc in DuraLith. It is essential to elucidate these factors for better understanding and modeling the long-term contaminant release mechanisms of COCs. Applying spectroscopic techniques, such as extended absorption fine structure (EXAFS), X-ray absorption near edge structure (XANES), and nuclear magnetic resonance (NMR) are needed to understand the precise bonding information, such as the coordination numbers and the bonding distance between the central and the nearest neighboring elements, the redox state, and the identity of COCs.

6.3 Contaminant Release Mechanisms

Currently, contaminant release mechanisms are unknown for DuraLith waste forms. Contaminant release from waste forms are a function of reactive surface area, porosity, degree of carbonation of the material, the moisture content, and the temperature of the disposal environment. Therefore, appropriately designed tests are used to generate data for predicting contaminant release. Initial performance testing can be conducted at bench-scale to obtain the critical model parameters under a compressed time-scale. Two of such tests are 1) SPFT and 2) PUF. The parameters from these tests can be input into appropriate PA models to predict waste form performance for products such as the DuraLith process over the life-span of the repository (McGrail et al. 2003).

7.0 Waste Acceptance Criteria

Waste acceptance criteria are a set of conditions the waste forms must meet to be accepted for disposal at a repository. Following is a set of requirements specified for solid radioactive waste forms.

7.1 Void Space

Void space measurements data for scaled-up monoliths are not currently available. These data will be available once the engineering-scale monolith task is completed.

7.2 Surface Dose Rate

Proposed dose rate limits for wastes to be accepted into the IDF include a constraint that containers have surface dose rates less than or equal to 2 millisievert per hour (200 millirem per hour) at contact and less than 1 millisievert per hour (100 millirem per hour) at 30 centimeters (11.8 inches) (RPP 2005). As part of a conceptual design report for a Supplemental Treatment Unit to be added to ETF, a dose calculation was performed as input to the design of the facility (*Conceptual Design Report for Effluent Treatment Facility Solidification Treatment Unit*, HNF-26914). The dose rate calculation considered liquid waste streams from WTP, DB3, supplemental treatment using bulk vitrification, and Basin 42. A 4-foot × 4-foot × 4-foot concrete block with a specific density of 1.5 g/mL was assumed as the waste form. The specific density is conservative because more dense materials provide more shielding. There is no indication whether the calculation included a container for the waste form block. The highest dose rate was from radionuclides in the DB3 waste stream.

A dose rate of 1.25 millirem per hour (0.0125 millisievert per hour) was calculated at 1 inch from the block side, and 0.75 millirem per hour (7.5 microsievert per hour) was calculated at 1 foot from the side of the waste form block for the DB3 solidified waste.

The ETF will not accept wastes for treatment with radionuclide concentrations above its design basis per administrative controls. Once treated and solidified in ETF, each final waste container cannot exceed the IDF dose rate limit constraints (see above).

7.3 Free Liquids

The Paint Filter Liquids Test (EPA SW 846 Method 9095B) is used to determine the presence of free liquids in a representative sample of solid waste. This method is used to confirm that the solids comply with 40 CFR 264.314 and 265.314 regulations for waste disposal. In brief, the method consists of taking a known weight amount of sample and placing it a mesh number 60 ±5% paint filter. If any portion of the material passes through and drops from the filter within the 5-min test period, the material is deemed to contain free liquids. Samples of DuraLith materials cured for 7 days were recently tested by Gong et al. (2011) and found to pass this test. The results are shown in Table 7.1.

Table 7.1. Results of the Free Liquids Test

Sample	Sample Mass (g)	Free Water
S1-4X5	100.25	No
S1-4X5 Duplicate	100.58	No
S1-6X5	100	No
S1-6X5 Duplicate	100	No
S1-6X6	100	No
S1-6X6 Duplicate	100	No

All samples were tested after 7 days of curing.

7.4 Dangerous Waste Limitations

Currently, the results of the TCLP (EPA Method 1311) and ANSI/ANS-16.1 leach test are used to assess whether a waste form meets the regulatory requirements for leachability of COCs. These two tests have been conducted on one set of DuraLith specimens prepared using HSW (2005) simulant and more recently on another set of optimized DuraLith samples prepared using the HSW S1 simulant. Brief descriptions of these two regulatory test methods and the results of these tests are presented in the following sections.

7.4.1 Toxic Characteristic Leaching Procedure (EPA Test Method 1311)

The TCLP is the current regulatory test procedure (EPA 2000) used to confirm whether a solid waste, including waste forms that are destined for disposal at a waste repository, will meet the restrictions associated with several regulated hazardous metals and selected regulated organic compounds. This test is conducted to make sure that the waste forms meet the requirements described for land disposal facilities (40 CFR 268). Following is a brief synopsis of the TCLP EPA 1311 method and a tabulation of results obtained for DuraLith polymeric waste forms.

For wastes containing greater than or equal to 0.5% solids, the liquid, if any, is separated from the solid phase and stored for later analysis; the particle size of the solid phase is reduced, if necessary. The solid phase is extracted with an amount of extraction fluid equal to 20 times the weight of the solid phase. The extraction fluid used is a function of the alkalinity of the solid phase of the waste. Particle-size reduction is required, unless the solid has a surface area per gram of material equal to or greater than 3.1 cm^2, or is smaller than 1 cm in its narrowest dimension (i.e., is capable of passing through a 9.5-mm (0.375 in.) standard sieve). If the surface area is smaller or the particle size larger than described above, the solid portion of the waste is prepared for extraction by crushing, cutting, or grinding the waste to a specific surface area or particle size. The extraction vessel containing the solid/solution mixture is then rotated at 30 ±2 rpm for 18 ±2 hours at 23 ±2°C. Following the extraction, the material in the extractor vessel is separated into its component liquid and solid phases by filtering it through a new glass fiber filter. After collecting the TCLP extract, the pH of the extract is recorded. An aliquot of the extract is taken for analysis. The aliquots must be acidified with nitric acid to pH <2. If any precipitation is observed after adding nitric acid to a small aliquot of the extract, then the remaining portion of the extract for metals analyses is not acidified, and the extract is analyzed as soon as possible. All other aliquots must be stored under refrigeration (4°C) until analyzed.

The results of the TCLP tests conducted on different formulations of DuraLith polymeric waste forms are listed in Table 7.2. The data indicate that the concentrations of the RCRA constituents (Ag, As, Cd, Cr, Hg, and Pb) in the leachates from all DuraLith samples tested were well below the UTS regulatory limits.

7.4.2 ANSI/ANS 16.1 Leach Test—Leachability Index

The ANSI/ANS-16.1-2003 test (ANSI 1986) is a 90-day semi-dynamic leach experiment that consists of submerging a monolithic sample (with a fixed geometry) in DIW at a fixed liquid, volume-to-solid surface area ratio and sampling at fixed periods of time.

The geometric surface area is used in this test method and calculated based on the cylindrical dimensions of the sample. The average calculated geometric surface area was 201.5±0.5 cm^2. At each of the 10 pre-determined leaching intervals, the leaching solution is exchanged with fresh leachant (DIW). The cylindrical monolith sample (2-inch diameter by 4-inch height) was placed into the center of a leaching vessel and mixed with DIW to maintain a leachant, volume-to-sample, surface area of 10 ±0.2 (cm). The sample stand and holder were used to maximize the contact area of the sample with the leaching solution. In between the sampling/replacement intervals, the experimental vessels were covered with a lid. The leaching times at which solution exchanges were made for these experiments were 2, 7, and 24 hours and 2, 3, 4, 5, 19, 47, and 90 days. Leachate samples collected during these intervals were stored in screw top containers with minimal head space under refrigeration until the entire batch of collected samples was submitted for chemical analysis.

The effective diffusivity calculated based on a semi-infinite solid and is defined as:

$$D = \pi \left[\frac{(a_n / A_o)}{(\Delta t)_n} \right]^2 \left(\frac{V}{S} \right)^2 T \tag{7.1}$$

where D = effective diffusivity (cm^2/s)
V = volume of specimen (cm^2)
S = geometric surface area of the specimen as calculated from measured dimensions (cm^2)
T = leaching time representing the "mean time" of the leaching interval (s)
a_n = quantity of a given element released from the specimen during the leaching interval n
A_o = total quantity of a given element in the specimen at the beginning of the first leaching interval
Δt_n = duration of the n'th leaching interval (s)
T = $[½(t_n^{½} + t_{n-1}^{½})]^2$

Alternately, the observed diffusivity for each constituent can be calculated using the analytical solution, Equation 6.1, for simple radial diffusion from a cylinder into an infinite bath as presented by Crank (1986).

The mean observed diffusivity for each constituent can be determined by taking the average of the interval observed diffusivity with the standard deviation.

The LI, the parameter derived directly from immersion test results, evaluates diffusion-controlled contaminant release with respect to time. The LI is used as a performance criterion to assess whether a stabilizing waste form is likely to be acceptable for subsurface burial and disposal in the target waste repository. In most cases, the immobilizing waste form is considered effective when the LI value is equal to or greater than nine. The LI is calculated by Equation 7.3.

$$LI_n = -Log(\frac{D_n}{cm^2 / s}) \tag{7.2}$$

where LI_n is the Leachability Index, and D_n is the effective diffusivity (cm^2/s) for components of interest during the leach interval *n*.

The results of the ANSI/ANS-16.1 tests conducted on different formulations of DuraLith polymeric waste forms are listed in Table 7.3. The data indicated that values of LI for Re (as a Tc surrogate) range from 9.62 to 10.59 for DuraLith samples prepared from HSW and SBW simulants in 2005 and from ~8.06 to 10.81 for optimized DuraLith samples prepared using HSW S1 simulant and tested in 2010. It is important to note that Re and Tc have different redox potentials that can affect the application of Re as an appropriate Tc surrogate in waste forms that contain reductive components such as Sn (II) compounds and/or BFS. For these latter samples, the calculated LI values for Na ranged from 8.51 to 9.59. The LI values for I were not determined. However, the LI values for I for samples prepared in 2005 ranged from 3.93 to 4.12.

Table 7.2. Results of TCLP Tests on DuraLith Specimens

Waste Type/Loading	Actual Waste/Simulant Spikes	Sample Preparation	Tests	Leachate Conc (mg/L)						Reference
HSW (2005)	Simulant Re and I spiked	VSL-CUA	PNNL	Ag : <0.07 Cd: <0.03 Cr: 0.04; Hg: <0.01 Pb: <0.10						Russell et al. (2006)
SBW (2005)	Simulant Re and I spiked	VSL-CUA	PNNL	Ag : <0.07 Cd: <0.03 Cr: 0.01; Hg: <0.01 Pb: <0.10						Russell et al. (2006)
HSW S1 (2010)	Simulant Re and I spiked	VSL-CUA Water Optimization Samples	VSL-CUA	Sample	Ag	As	Cd	Cr	Pb	Gong et al. (2011)
				S1-2X2A	<0.07	<0.20	<0.03	0.01	0.12	
				S1-2X2B	<0.07	<0.20	<0.03	0.02	0.12	
				S1-2X3	<0.07	<0.20	<0.03	0.02	0.13	
				S1-2X5	<0.07	<0.20	<0.03	<0.01	0.15	
				S1-2X8	<0.07	<0.20	<0.03	<0.01	0.19	
				S1-2X10R	<0.07	<0.20	<0.03	<0.01	0.3	
				S1-2X12	<0.07	<0.20	<0.03	0.02	0.18	
				S1-2X13	<0.07	<0.20	<0.03	0.01	<0.10	
				S1-2X14*	<0.07	<0.20	<0.03	0.02	0.23	
				S1-2X15	<0.07	<0.20	<0.03	0.01	<0.10	
HSW S2, S3, S4 2M Na (2010)	Simulant Re and I spiked	VSL-CUA S2, S3 and S4 Simulant samples	VSL-CUA	Sample	Ag	As	Cd	Cr	Pb	Gong et al. (2011)
				S2-2X1	<0.07	<0.20	<0.03	0.01	0.11	
				S2-2X4	<0.07	<0.20	<0.03	0.02	0.21	
				S2-2X4R	<0.07	<0.20	<0.03	0.02	0.16	
				S3-2X1R	<0.07	<0.20	<0.03	0.01	0.11	
				S3-2X2R	<0.07	<0.20	<0.03	0.02	0.26	
				S4-2X1	<0.07	<0.20	<0.03	0.02	0.19	
				S4-2X4	<0.07	<0.20	<0.03	0.03	0.32	
HSW S1 (2010)	Simulant Re and I spiked	VSL-CUA Combination of Enhances and other additives	VSL-CUA	Sample	Ag	As	Cd	Cr	Pb	Gong et al. (2011)
				S1-2X12R1	<0.07	<0.20	<0.03	0.01	0.25	
				S1-2X12R2	<0.07	<0.20	<0.03	0.01	0.23	
				S1-2X13R1	<0.07	<0.20	<0.03	<0.01	0.14	
				S1-2X13R2	<0.07	<0.20	<0.03	<0.01	0.11	
				S1-2X18	<0.07	<0.20	<0.03	0.01	0.16	
				S1-2X19	<0.07	<0.20	<0.03	0.02	0.12	
				S1-2X12R1	<0.07	<0.20	<0.03	0.01	0.25	

Table 7.2. (contd)

Waste Type/Loading	Actual Waste/Simulant Spikes	Sample Preparation	Tests	Leachate Conc (mg/L)						Reference
HSW S1 (2010)	Simulant Re and I spiked	VSL-CUA Robustness Test Samples	VSL	Sample	Ag	As	Cd	Cr	Pb	Gong et al. (2011)
				S1-2XV1*	<0.07	<0.20	<0.03	0.02	0.21	
				S1-2XV2	<0.07	<0.20	<0.03	0.02	0.22	
				S1-2XV4	<0.07	<0.20	<0.03	0.02	0.19	
				S1-2XV5	<0.07	<0.20	<0.03	0.02	0.19	
				S1-2XV6	<0.07	<0.20	<0.03	0.01	0.16	
				S1-2XV7	<0.07	<0.20	<0.03	0.01	0.14	
				S1-2XV8	<0.07	<0.20	<0.03	0.01	0.16	
				*Baseline sample						
HSW S1 (2010)	Simulant Re and I spiked	VSL-CUA Higher Waste loading samples	VSL	Sample	Ag	As	Cd	Cr	Pb	Gong et al. (2011)
				S1-8X1	<0.07	<0.20	<0.03	<0.01	<0.10	
				S1-8X2	<0.07	<0.20	<0.03	<0.01	<0.10	
				S1-8X1R*	<0.07	<0.20	<0.03	<0.01	<0.10	
				S1-8X2R*	<0.07	<0.20	<0.03	<0.01	<0.10	
				S1-5X1*	<0.07	<0.20	<0.03	<0.01	0.15	
				S1-5X2*	<0.07	<0.20	<0.03	<0.01	0.14	
				S1-6X1R*	<0.07	<0.20	<0.03	<0.01	0.13	
				S1-6X2R*	<0.07	<0.20	<0.03	<0.01	0.12	
				S1-4X1R3	<0.07	<0.20	<0.03	<0.01	0.16	
				S1-4X2R1	<0.07	<0.20	<0.03	0.01	0.15	
				*Doped with Water Reducer 800 – 1200 ml/100 kg dry product						

Universal Treatment Standards (UTS) Limits
Ag: 0.14 mg/L
As: 5.00 mg/L
Cd: 0.11 mg/L
Cr: 0.60 mg/L
Hg: 0.025 mg/L
Pb: 0.75 mg/L.

Table 7.3. LI Data from ANS/ANSI 16.1 Tests on DuraLith Samples

Waste Type/Loading	Actual Waste/Simulant Spikes	Monolith	Test	Leachability Index	Reference
HSW (2005)	Simulant Re and I spiked	Prepared by VSL-CUA	Conducted by PNNL	VSL/HSW-TB-9R3B-S-3: Na 8.62, Re 10.59, I 4.12 VSL/HSW-TB-9R3E-S-5: Na 8.59, Re 10.18, I 2.37	Russell et al. (2006)
SBW (2005)	Simulant Re and I spiked	Prepared by VSL-CUA	Conducted by PNNL	VSL/HSW-TB-9R3B-S-3: Na 8.34, Re 9.62, I 4.65 VSL/HSW-TB-9R3E-S-5: Na 7.74, Re 9.88, I 3.93	Russell et al. (2006)
HSW S1	Simulant Re and I spiked	Prepared by VSL-CUA	Conducted by VSL-CUA	Sample Na Re S1-2X13R2-7-L01 9.59 10.13 S1-2X13R2-7-L02 9.33 10.63 S1-2X13R2-7-L03 9.32 10.81 S1-2X13R2-7-L04 9.20 9.26 S1-2X13R2-7-L05 9.20 8.22 S1-2X13R2-7-L06 8.51 8.06 S1-2X13R2-7-L08 8.72 9.30 S1-2X13R2-7-L09 8.61 9.45 S1-2X13R2-7-L10 8.66 9.55 S1-2X14-L01 9.49 9.84 S1-2X14-L02 9.16 9.24 S1-2X14-L04 9.04 9.79 S1-2X14-L08 9.49 9.45 S1-2X14-L09 9.30 9.27 S1-2X14-L10 9.43 9.37	Gong et al. (2011)

7.5 Compressive Strength

The compressive strength tests are typically conducted with the American Society for Testing and Materials (ASTM) Standard Procedure C-39/C39M (ASTM 2010), which is used to determine the compressive strength of cylindrical samples. Compressive-strength values of tested DuraLith monoliths typically depend on the size and shape of the sample, the batching, the mixing procedures, and the methods of sampling, molding, and fabrication as well as the age, temperature, and moisture conditions during curing. Compressive strength tests on waste monoliths may also be conducted after thermal cycling, exposure to radiation, and immersion in water to assess the impact of each of these treatments.

According to the test method, a sample is loaded into the testing apparatus so that the axis of the specimen is aligned with the center of thrust of the spherically seated block of the testing apparatus. Before testing the specimen, the load indicator is set to zero. The loading is applied continuously without any shock at a stress rate of 0.25 ± 0.05 MPa/s (35 ± 7 psi/s). The designated rate of movement should be maintained at least during the latter half of the anticipated loading phase. The loading is maintained until the load indicator starts to decrease steadily, and the specimen displays a well-defined fracture pattern as illustrated in the C-39/C39M test method. The compressive strength is calculated by dividing the maximum load imposed on the specimen during the test by the average cross sectional area. The result is typically expressed to the nearest 0.1 MPa (10 psi).

Compressive strength tests have been conducted on irradiated and non-irradiated DuraLith formulations by Russell et al. (2006). The fracture modes observed for these specimens are shown in Figure 7.1. All Monoliths show a Type 3 Fracture Pattern. Recently, compressive strength tests of HSW optimized DuraLith cylinders (2 in. diameter and 4 in. tall) that were cured for 28 days were conducted by Gong et al. (2011). The results of the tests are listed in Table 7.4.

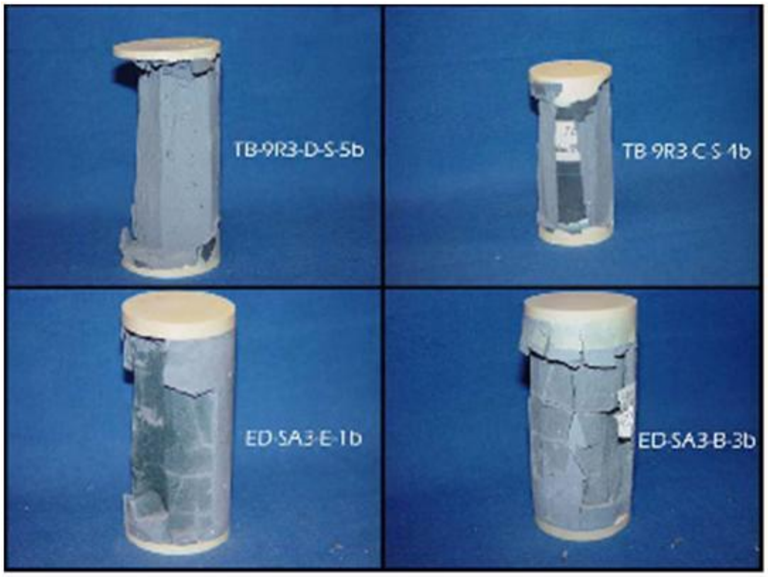

Figure 7.1. Compressive Strength Test Failure Modes of DuraLith Monoliths (Russell et al. 2006)

Table 7.4. Compressive Strength Data for DuraLith Cylinders

Waste Type/Loading	Actual Waste/Simulant Spikes	Monolith	Test Method	Compressive Strength	Reference
HSW (2005)	Simulant Re and I spiked	Prepared by VSL-CUA	ASTM C39 – 2005	Irradiated:[(a)] 29.1 ±8.1 MPa (4230 ±1171 psi) Non-radiated: 27.5 ±4.0 MPa (3990 ±578 psi)	Russell et al. (2006)
SBW (2005)	Simulant Re and I spiked	Prepared by VSL-CUA	ASTM C39 – 2005	Irradiated:[(a)] 26.0 ±2.8 MPa (3780 ±400 psi) Non-radiated: 26.6 ±3.5 MPa (3850 ±315 psi)	Russell et al. (2006)
HSW S1(2010)	Simulant Re and I spiked Specimen compositional variations: ±10 % mass variations in ingredients such as, MK, FS, KOH and silica fume. Baseline specimens: S1-2XV0 and S- 2XV1	Prepared by VSL-CUA	ASTM C39/C 39M (2010)	S1-2XV0: 143.8 MPa (20865 psi) S1-2XV1: 156.2 MPa (22667 psi) S1-2XV1R: 130.8 MPa (18983 psi) S1-2XV2: 154.6 MPa (22439 psi) S1-2XV3: 142.0 MPa (20608 psi) S1-2XV4: 136.0 MPa (19738 psi) S1-2XV5: 143.0 MPa (20755 psi) S1-2XV6: 147.3 MPa (21380 psi) S1-2XV7: 115.5 MPa (16757 psi) S1-2XV8: 133.8 MPa (19420 psi)	Gong et al. (2011)

(a) Total dose for each specimen: 1.0E+8 Rad

8.0 Summary of Key Waste Attributes

DuraLith is an alkali-activated geopolymer waste form developed by Vitreous State Laboratory-Catholic University of America (VSL-CUA) for encapsulating liquid radioactive waste. A DuraLith waste form developed for treating Hanford secondary waste liquids is prepared by alkali-activation of a mixture of ground blast furnace slag and metakaolinite with sand used as a filler material. The process consists of adding a mixture of alkalis (KOH and NaOH) and silica fume to the liquid waste to produce an activator solution. A small amount of tin compound is added to the waste solution to reduce Tc(VII) into less soluble Tc(IV). Next, the activator solution is blended into the dry ingredient mixture consisting of blast furnace slag, metakaolin, and a limited quantity of silver zeolite. The latter ingredient is added to precipitate radioiodine, thus decreasing its leachability from the waste form. The salient characteristics and the results of performance testing of the DuraLith waste form are summarized here:

Based on process optimization tests, solid waste loading of ~7.5% and ~14.7 % has been achieved using the Hanford secondary waste S1 and S4 simulants, respectively. The Na loading in both cases is equivalent to ~6 M.

Continuous mixing of activator for a period of ~24 hours needed for confirming complete dissolution of silica fume.

Small amounts of elemental silicon contained in the silica fume can result in hydrogen evolution from the activator solution as the silica fume is dissolved. Alternative silica sources (e.g., potassium silicate hydrate) may be used to mitigate this problem.

Heat is generated when the activator solution is prepared because alkali dissolution of silica fume is an exothermic reaction. For a 7-kg batch, a peak temperature of ~67°C has been observed at 9 hours of reaction time. Therefore, the activator solution tanks need to be equipped with cooling coils to keep the temperature at ~45°C.

Heat is also generated when the activator solution is blended into the dry ingredient mix to initiate the polymeric reaction. Peak temperatures approaching ~107°C have been noted for a 5-kg batch of DuraLith paste at 90 minutes of curing. Use of Class F fly ash in the mix may reduce the peak temperatures.

A working time window of ~20 minutes between the time when mixing is complete, and the time when the process of pouring the DuraLith into the molds is finished. If the casting window is exceeded, the mix is difficult to pour, and the resulting monolith may turn out to be more porous. Working time window can be extended to ~30 minutes if Class F fly ash is substituted for 75% of metakaolin and blast furnace slag in the mix.

A preliminary DuraLith process flow sheet has been developed by VSL-CUA for processing Hanford secondary waste. According to this basin design, 10 to 22 waste monoliths (each 48 ft^3 in volume) can be produced per day, depending on the degree of waste concentration before mixing. There are no current pilot-scale or full-scale DuraLith plants under construction or in operation; therefore, the cost of DuraLith production is unknown.

Results of the non-regulatory leach tests (EPA Draft 1313 and 1316) of Waste Simulant S1-optimized DuraLith specimens indicated that the concentrations of RCRA metals (Ag, Cd, Cr, Hg, and Pb) in the leachates were well below the limits set by the Universal Treatment Standards (UTS) specified in 40 CFR 268.48). The data from the EPA draft 1315 leach test showed that leachability index (LI) values for contaminants of concern (COCs), namely ^{99}Tc and I, ranged from 8.2 to 11.4 and 4.3 to 7.5, respectively.

Results of the regulatory leach test (Toxicity Characteristic Leach Procedure, EPA Method 1311) conducted on Waste Simulant S1-optimized DuraLith specimens indicated that the concentrations of RCRA metals (Ag, As, Cd, Cr, Hg, and Pb) in the leachates were well below the UTS 40 CFR 268.48 limits). The data from the ANSI/ANS 16.1 leach test showed that LI values for one COC, namely Re (as a Tc surrogate), ranged from 8.06 to 10.81. The LI value for another COC, namely I, was not measured in this test.

The results of the compressive strength testing of Waste Simulant S1-optimized DuraLith specimens indicated that the specimens were physically robust with compressive strengths ranging from 115.5 MPa (16757 psi) to 156.2 MPA (22667 psi).

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Appendix A

Supplemental Treatment Technology Selection Decision Goals, Criteria, Measures, Technology Issues, and Testing Objectives

Table A.1. Supplemental Treatment Technology Selection Decision Goals, Criteria, and Measures[(a)]

Goal	Criterion	Measures	Data Package Contents
Ensure worker and public safety	Achieve inherently safe system	Independent safety expert assessment	Process description, equipment description, process temperatures, hazardous chemicals, worker dose, hydrogen generation, process effluents, flammable gases
Provide environmental protection comparable to current vitrified waste disposal plan	Waste form performance	Flux at points of undisturbed soil and bottom of the waste packages	See next table
	Disposal space required	Acres of land for disposal site	Waste loading, density, package design
	Secondary wastes produced	Potential to emit (PTE) constituents: solid waste volume, liquid waste volume	Process description, flowsheet description, off-gas generation, and secondary wastes expected
Maximize schedule acceleration	Confidence in meeting 2028 date	50% probability data for achieving 10 gallons per minute (gpm) throughput	Unknown
	Process robustness	Metric tons of sodium (Na) processed by 2028	Range of wastes compositions tested, waste loading range, concentration (water content), sodium molarity
Maximize cost effectiveness	Life cycle cost	Life cycle cost	Process description, flowsheet description, off-gas generation, and secondary wastes expected, dry materials description. Reference/cite cost data if located in literature
	Peak year cost	Peak year cost	Process description, flowsheet description, off gas generation, and secondary wastes expected, dry materials description

Table A.1. (contd)

Goal	Criterion	Measures	Data Package Contents
Maximize operability	Operability risk	Independent expert assessment to include: number of unit operations; equipment count, etc.	Process description, flowsheet description
Minimize overall system interface impacts	System interface impacts	Liquid effluent greater that ETF capacity	Secondary waste is at back end. ETF upgrade to provide capacity
		Dose of waste package (impacting handling within disposal system	Not applicable
		Volume returned to double-shell tanks (DSTs)(impacting stored waste volume)	Not applicable

(a) Raymond RE, RW Powell, DW Hamilton, WA Kitchen, BM Mauss, and TM Brouns. 2004. *Initial Selection of Supplemental Treatment Technologies for Hanford's Low-Activity Tank Waste*. RPP-19763, WM-04, Waste Management Conference, February 29-March 4, Tucson, Arizona.

Table A.2. Summary of Testing Recommendations for Containerized Grout Technology—Waste Form Performance[(a)]

Technical Issue/Uncertainty	Testing Objective	Specific Testing	Data Package Content
Data on nitrate/nitrite and Cr release rates from test samples to meet PA data needs	Optimize grout formulation to provide highest waste loading with lowest release rate. Performance on nitrate/nitrite likely to be limiting factor on waste loading.	Prepare grout samples and conduct leach tests (ANSI/ANS 16.1) with samples that have cured for a maximum of 28 days. Report leach rates for nitrate/nitrite and Cr at 5 days, but continue to collect data for full 90 days.	Leach Data including ANSI/ANS 16.1, EPA 1315, ASTM 1308. Location of contaminants within waste form phases, mechanisms of containment, mechanisms of release, dissolution of waste form phases, diffusion coefficients/leachability index for Cr, nitrate, nitrite
	Determine waste loading/performance relationship (until a target for release rate is set, the relationship is more important than determining a waste loading that meets a criterion.)	Prepare grout samples from simulants with waste loadings that vary over at minimum of 3X (e.g., 10 to 30% or 1 to 3%). Conduct leach tests as per above.	Impact of waste loading on leaching. Identify constituents impacting waste loading and waste form setting
Retention of Tc, U, and I as a function of waste loading	Gather enough Tc, U, and I release rate data to meet PA data needs	Prepare grout samples and conduct leach tests (ANSI/ANS 16.1) with samples that have cured for a maximum of 28 days. Report leach rates for Tc, U, and I at 5 days, but continue to collect data for full 90 days.	Leach Data including ANSI/ANS 16.1, EPA 1315, ASTM 1308. Location of contaminants within waste form phases, mechanisms of containment, mechanisms of release, dissolution of waste form phases, diffusion coefficients/leachability index for Tc, I, and Re.
	Determine waste loading/ performance relationship (until a target for release rate is set, the relationship is more important than determining a waste loading that meets a criterion.)	Prepare grout samples from simulants with waste loadings that vary over at minimum of 3X (e.g., 10 to 30% or 1 to 3%). Conduct leach tests as per above.	Impact of waste loading on leaching. Identify constituents impacting waste loading and waste form setting

Table A.2. (contd)

Technical Issue/Uncertainty	Testing Objective	Specific Testing	Data Package Content
Identification of constituents that might be poorly retained by grout and may impact permitting	Determine other key risk drivers and make suitable measurements to support calculations/models. RCRA metals, other radionuclides (e.g., Cs), all listed waste constituents (series of codes for solvents F001-F005), LDR organics and inorganics, and criteria metrics-fish bioassay.	Take leachate solutions from the testing on waste forms generated with actual waste and analyze for all constituents shown to be in the waste at levels of concern. Both ANSI/ANS 16.1 and TCLP leachates will be tested.	RCRA metals, nitrates, nitrites, chlorides, fluorides, organics, etc. in wastes and in waste form dry materials. TCLP, fish test
Validity of simulant testing	Demonstrate that simulant and actual waste release rates match.	At loading suggested by vendor, produce three waste form samples from simulated waste and three from actual waste. Conduct leach tests (ANSI/ANS 16.1) on each simulant and actual waste set cured under identical conditions. Samples must cure for a maximum of 28 days. Report leach rates for nitrate/nitrite, Cr, Tc, U, and I at 5 days but continue to collect data for full 90 days.	Don't expect to see any data on actual secondary wastes. Look at work done with actual LAW wastes.
		At loading suggested by vendor, produce a fourth waste form sample from simulated waste and another from actual waste. Conduct TCLP tests on sample from simulant and sample from actual waste cured under identical conditions.	

Table A.2. (contd)

Technical Issue/Uncertainty	Testing Objective	Specific Testing	Data Package Content
	Verify that solidification materials locally available at the Hanford Site produce desired results.	Studies with formulations that use routine solidification agents such as cement and fly ash should use samples obtained from local sources to help assure that regional differences in solidification agents will not introduce potential consistency problems.	Identify and describe any work looking at alternative sources of dry materials.
Effects of mitigating features on environmental performance	Determine efficacy of proposed "getters"	Prepare grout samples and conduct leach tests (ANSI/ANS 16.1) with samples cured for a maximum of 28 days. Report leach rates for nitrate/nitrite and target COC (e.g., Tc) at 5 days; continue to collect data for full 90 days.	Summarize data on testing with getter materials. BFS, Ag zeolite, reductants, $SnCl_2$, etc. Compare with and without getters, short-term data and long-term performance
	Determine efficacy of mitigating features for preventing contaminants from leaving the disposal system.	Conduct accelerated disposal tests at conditions representative of the Hanford disposal site to show mitigated release of contaminants.	Any long-term test data. PCT, SPFT, PUF, EPA 1313, 1314, 1316.
	Estimate expected efficacy of proposed feature for long-term Hanford application.	Conduct accelerated disposal tests to identify operable range limits for proposed process	Any Hanford-specific long-term data. Otherwise out of scope (disposal facility design)
		Perform engineering evaluation on laboratory data from accelerated disposal test demonstration	
Data to support grout facility design	Collect grout curing and strength data	Determine the heat release per volume of grout and thermal conductivities of the proposed grouts.	Heat of curing, thermal conductivity, source of heat
		Measure grout strength as a function of curing temperature	Impact of curing temperature on waste form performance

Table A.2. (contd)

Technical Issue/Uncertainty	Testing Objective	Specific Testing	Data Package Content
	Collect data on H_2 generation in container	Measure the H_2 generation for the final proposed grout formulation	Not an issue for secondary waste
	Collect data on amount of leachate generated as grout cures(or use existing data with engineering analysis if sufficient to address issue)	Estimate amount of leachate that is release during curing process	Identify any free liquids.
		Measure grout porosity	Provide any data or calculated values. Valuable data but may not directly impact down selection.

(a) Josephson GB, LM Bagaasen, JGH Geeting, PA Gauglitz, GJ Lumetta, and JS Tixier. 2003. *Hanford Mission Acceleration Initiative – Preliminary Testing Recommendations for Supplemental Treatment*. PNNL-14005 Rev. 1. Pacific Northwest National Laboratory, Richland, Washington.

Appendix B

Initial Draft Waste Form Selection/Waste Acceptance Criteria for Hanford WTP Secondary Waste Form

Appendix B

Initial Draft Waste Form Selection/Waste Acceptance Criteria for Hanford WTP Secondary Waste Form

The attached Table B.1 provides initial draft waste acceptance criteria and waste form selection criteria for secondary liquid wastes from the Hanford Tank Waste Treatment and Immobilization Plant (WTP). It is assumed that the secondary wastes will be treated and solidified in the Effluent Treatment Facility before disposal in the Integrated Disposal Facility (IDF). The criteria were developed originally in 2004 and were based on the Hanford Site Solid Waste Acceptance Criteria as well as the waste acceptance criteria for the immobilized low-activity waste glass waste form to be prepared in WTP for disposal in IDF. In 2004 and 2005 Integrated Disposal Facility Waste Acceptance Criteria were drafted (Burbank DA. 2005. *Waste Acceptance Criteria for the Immobilized Low-Activity Waste Disposal Facility*. RPP-8402 Rev. 1, CH2M HILL Hanford Group, Inc., Richland, Washington). The latest available version for this exercise is Rev. 1, dated February 23, 2005.

The first three columns provide the original secondary waste form requirements including the title of the requirement, the requirement itself, and the technical basis for the requirement. The fourth column provides the corresponding requirement from the IDF waste acceptance criteria. The fifth column identifies the data package content to address the requirement.

Table B.1. Initial Draft Waste Form Selection/Waste Acceptance Criteria for Hanford WTP Secondary Waste Form

Property	Requirement	Basis	IDF Waste Acceptance Criteria[(a)]	Data Package Content
1.2.2.1 Return Streams	There shall be no return streams from the secondary waste stabilization facilities.	The process should not generate off-gas effluents. Any "bleed" water from curing or set-up of the stabilizing material (e.g., grout or other material) can be mitigated by design.		Process description, flowsheet description
1.2.2.2 Package Description	The constituent parts of each package are a sealed metal container enclosing the stabilized secondary waste form and an optional filler material.	The disposal infrastructure planned in conjunction with the Integrated Disposal Facility (IDF) includes systems for handling cylindrical WTP canisters, solid waste drums and boxes, and potentially large (8 ft × 8 ft × 20 ft) roll-off boxes for the supplemental treatment waste form. The preferred option for SSW is to utilize one of the currently planned disposal system packages and corresponding interfaces. Use of a different container may be more efficient, but will have to be evaluated against the disposal system impacts.	4.3.1 Package Construction Containers must be made of or lined with materials that will not react with, and are otherwise compatible with, the dangerous waste during handling and storage before disposal such that the ability of the container to contain the waste is not impaired. Waste containers are limited to those constructed of noncombustible or fire retardant materials. Container materials will be limited to the following: • Metal, concrete, masonry • Other not listed here	Range of packages defined in IDF WAC. Provide description of waste form including chemical form

Table B.1. (contd)

Property	Requirement	Basis	IDF Waste Acceptance Criteria[(a)]	Data Package Content
1.2.2.3 Size and Configuration	Package size and configuration should be selected considering the disposal infrastructure at IDF and performance requirements and objectives. IDF will include capability to handle WTP canisters (304 stainless-steel right circular cylinder, 2.3 m high, and 1.22 m in diameter), standard 55-gal and 85-gal drums, and may include other larger containers.	See 1.2.2.2 Package Description	<u>4.3.2 Size</u> Only containers meeting the type, size and construction specified in this section have been evaluated for criticality safety. No other container types are approved for disposal at the IDF unless a criticality safety evaluation is performed. Type 2: LLW waste packaged in 208L (55-gal) drums Type 3: LLW waste packaged in 322L (85-gal) drums Type 4: LLW waste packaged in MB-V boxes measuring 1.2 m wide × 1.2 m high × 2.4 m long (4-ft × 4-ft × 8-ft) Type 5: LLW waste packaged in medium boxes greater than or equal to 3.95 m^3 but less than 15 m^3. The dimensions are not fixed. Type 6: LLW waste packaged in small boxes less than 3.95 m^3. The dimensions are not fixed.	Package size and configuration not expect to impact waste form selection

Table B.1. (contd)

Property	Requirement	Basis	IDF Waste Acceptance Criteria[(a)]	Data Package Content
1.2.2.4 Mass	The mass of each loaded package shall not exceed 85 metric tons.	The maximum mass is calculated considering the limitations (force per unit surface area) of the IDF liner system and transportation system. The 85-metric ton limit is specific to the footprint of the large metal roll-off boxes, and assumed they were fully loaded with supplemental ILAW glass.		Waste load and density
1.2.2.5 Closure and Sealing	A means of mitigating hydrogen generation shall be provided in the package closure design. A Nucfil 013™ filter (or equivalent) shall be used in combination with a hydrogen recombination catalyst to prevent loss of radionuclides from the container or hydrogen accumulation in the disposal configuration. Pouring a non-radioactive cold cap as a filler material is recommended.	Provide equivalence to HNF-EP-0063, Rev 10, Section 3.36, Gas Generation. Some level of radiolytic decomposition may occur in the SSW and hydrogen may evolve.	4.1.11 Gas Generation When waste is packaged, vents or other measures shall be provided if the potential exists for pressurizing or generating flammable or explosive concentrations of gases within the waste container.	Package closure and sealing not expected to be a factor in waste form selection
1.2.2.6 Labeling	Each package shall be labeled in accordance with the requirements of the Integrated Disposal Facility Waste Acceptance Criteria. (RPP-8402)	See 1.2.2.2 Package Description	4.3.5 Marking and Labeling Containers of LLW shall be marked such that their contents can be identified. Packages shall be labeled according to the instructions in Appendix C.	Package labeling not expected to be a factor in waste form selection

Table B.1. (contd)

Property	Requirement	Basis	IDF Waste Acceptance Criteria[(a)]	Data Package Content
1.2.2.7 Void Space	The void space in the container shall not exceed ten percent of the total internal volume at the time of filling with the SSW and optional filler material	Meets the requirements of Dangerous Waste Regulation, Washington Administratve Code (WAC) 173-303-665 (12); i.e., the container shall be at least ninety (90) percent full when placed in the landfill.	4.1.4 Solidification and Stabilization All containerized waste must fill at least 90 percent of the internal volume of the container when placed in the disposal unit.	Describe process demonstrations, bench, engineering, pilot, and full scale

Table B.1. (contd)

Property	Requirement	Basis	IDF Waste Acceptance Criteria[(a)]	Data Package Content
1.2.2.8 Radionuclide Concentration Limitations	The radionuclide concentration of the SSW shall not exceed levels corresponding to a waste category 3 as defined in the IDF WAC.	Meets the requirements of 10 CFR 61.55 and Hanford Site solid waste acceptance criteria.	<u>1.5 Waste Types Accepted for Disposal</u> The IDF will accept Low-Level Waste and Mixed Waste. LLW is radioactive waste that is not high-level radioactive waste, spent nuclear fuel, transuranic waste, byproduct material, or naturally occurring radioactive material. <u>4.2.1 Radiological Concentration</u> Radiological concentrations must meet all of the following conditions: • TRU content shall not exceed 100 nanocuries (3,700 becquerels) per gram of waste. • Waste category shall not excel Category 3. <u>4.2.2 Dose-Equivalent Curie Limits</u> The dose-equivalent curie (DE-Ci) for Category 1 waste cannot exceed 1 DE-Ci/m^3. The DE-Ci for Category 3 waste cannot exceed 107 DE-Ci/m^3. <u>4.2.3 Fissile Material Content</u> The fissionable material limit of any one container is restricted to 10 fissile gram equivalents per cubic foot of container volume.	Waste loading

Table B.1. (contd)

Property	Requirement	Basis	IDF Waste Acceptance Criteria[(a)]	Data Package Content
1.2.2.9 Radiological Composition Documentation	The radionuclide composition of the waste form shall be documented. Radionuclides shall be identified that are significant as defined in NUREG/BR-0204 and 49 CFR 172.101 (Table 2). Technetium-99 (^{99}Tc) shall be considered to be significant at concentrations greater than 0.003 Ci/m^3 in the SSW form. The inventories shall be indexed to December 31, 2002. The documentation shall be consistent with the radiological description format described in NUREG/BR-0204.	Equivalent to WTP approach for ILAW	4.2.1 Radiological Concentration Radionuclide concentrations must be reported in accordance with Appendix A.	Project record. Not part of data package
1.2.2.10 Surface Dose Rate Limitations	The dose rate at any point on the external surface of the package shall not exceed 2 millisievert per hour (200 millirem per hour) at contact and 1 millisievert per hour (100 millirem per hour) at 30 cm (11.8 inches)	Interface with the disposal system	4.2.6 Dose Rate Limits Containers with dose rates less than or equal to 2 millisievert per hour (200 millirem per hour) at contact and less than 1 millisievert per hour (100 millirem per hour) at 30 cm (11.8 inches) are acceptable.	Get WRPS hazard analysis. Waste loading
1.2.2.11 Surface Contamination Limitations	Removable contamination on the external surfaces of the package shall not exceed 367 Bq/m^2 for alpha and 3670 Bq/m^2 for beta-gamma contamination when measured using the method described in 49 CFR 173.443(a).	Interface with the disposal system	4.2.4 Package Removable Contamination Removable contamination on accessible surfaces of waste packages shall not exceed the limits of HNF-5183, *Tank Farm Radiological Control Manual*.	Process description, flowsheet description

Table B.1. (contd)

Property	Requirement	Basis	IDF Waste Acceptance Criteria[(a)]	Data Package Content
1.2.2.12 External Temperature	The temperature of the accessible external surfaces of the package shall not exceed 50°C when returned to DOE. This temperature constraint shall assume a shaded, still air environment at an ambient temperature of 38°C	Interface with the disposal system	4.1.13 Heat Generation Waste must not generate excess heat that would compromise the integrity of both contained and nearby wastes. If heat generation from radiological decay in the waste package exceeds 4.1 watts per cubic meter (0.1 watt per cubic foot), the package must be evaluated to ensure that the heat does not affect the integrity of the container or surrounding containers. The maximum temperature is limited by the 71.1ºC allowable design temperature at the primary geomembrane.	Radiogenic heat is not an issue. Document heat of curing. Curing time, set time.

Table B.1. (contd)

Property	Requirement	Basis	IDF Waste Acceptance Criteria[(a)]	Data Package Content
1.2.2.13 Free Liquids	The package shall contain no detectable free liquids as defined in ANSI/ANS-55.1 or SW-846 Method 9095	Compliance with 10 CFR Part 61	<u>4.1.3 Liquids and Liquid Containing Wastes</u> Liquid waste must be solidified or packaged in sufficient absorbent material to absorb twice the volume of liquid. Liquid waste or wastes containing liquids must be converted into a form that contains as little free-standing and non-corrosive liquid as is reasonably achievable, but in no case shall the liquid exceed 1% of the volume of the waste when the waste is in a disposal container designed to ensure stability, or 0.5% of the volume after it is processed to a stable form. For waste that has the potential for free liquid formation, the absence or presence of free liquids in the waste must be demonstrated using the following test method: Method 9095 (Paint Filter Liquids Test) as described in EPA Publication SW-846.	Document free liquids in laboratory and scale testing. Under what conditions were free liquids observed.

Table B.1. (contd)

Property	Requirement	Basis	IDF Waste Acceptance Criteria[(a)]	Data Package Content
1.2.2.14 Pyrophoricity or Explosivity	The package contents shall not be pyrophoric, readily capable of detonation, or readily capable of explosive decomposition or reaction (including reaction with water) at normal pressure and temperature. The waste form and any optional filler materials shall not be ignitable or reactive as defined in WAC 173-303-090(5) and WAC 173-303-090(7).	Compliance with WAC.	<u>4.1.9 Explosives</u> Waste must not be readily capable of detonation or of explosive decomposition or reaction at anticipated pressures and temperatures, or of explosive reaction with water. <u>4.1.10 Pyrophoric Wastes</u> Pyrophoric materials contained in the waste shall be treated, prepared, and packaged to be nonflammable.	Describe waste form including chemistry and starting materials.
1.2.2.15 Explosive or Toxic Gases	The loaded package shall not contain or be capable of generating quantities of explosive (e.g., hydrogen) or toxic gases, vapors, or fumes harmful to persons handling the waste.	SSW may generate radiolytic hydrogen that must be accounted for in the design.	<u>4.1.11 Gas Generation</u> Waste must not contain, or be capable of generating quantities of toxic gases, vapor, or fumes harmful to the public, workers, or disposal facility personnel, or harmful to the long-term structural stability of the disposal site.	Describe waste form including chemistry and starting materials. Radiogenic hydrogen is not expected to be an issue with secondary wastes. Decide how to address ammonia in SBS recycle.

Table B.1. (contd)

Property	Requirement	Basis	IDF Waste Acceptance Criteria[(a)]	Data Package Content
1.2.2.16 Dangerous Waste Limitations	The loaded package shall be acceptable for land disposal under the State of Washington Dangerous Waste Regulations, WAC 173-303, and RCRA LDR in 40 CFR Part 268. The waste form shall undergo full analysis of all constituents for applicability to these regulations, including testing using the Toxicity Characteristic Leaching Procedure (TCLP: SW-846, Method 1311) to ensure that limits for regulated metals are met.	Compliance with applicable Washington State and federal RCRA requirements.	4.1.1 Hazardous Waste The IDF will accept waste with the following dangerous waste numbers: D001, D002, D003, D004 through D043, State only (WT01, WT02, WP01, WP02, WP03, WSC2, and W001), and listed waste from non-specific sources (F001 through F012, F19, F028, and F039) and all "U" and "P" dangerous waste numbers. 4.1.2 Land Disposal Restrictions All waste subject to the Resource Conservation and Recovery Act of 1976 LDR) (40 CFR Part 268) and/or Washington State LDR (WAC 173-303-140) must be demonstrated to meet all applicable treatment standards and requirements. Waste not meeting LDR treatment standards will not be accepted.	TCLP, pH, describe waste form chemical composition, hazardous constituents in dry materials.

Table B.1. (contd)

Property	Requirement	Basis	IDF Waste Acceptance Criteria[(a)]	Data Package Content
1.2.2.17 Compressive Strength	The mean compressive strength of the waste form (and any optional filler material) shall be determined by testing representative non-radioactive samples. The compressive strength shall be at least 3.45E6 Pa when tested in accordance with ASTM C39/C39M-99 or an equivalent testing method.	NRC Branch Position Paper. *Technical Position on Waste Form.*	4.1.4 Solidification and Stabilization A solid waste must have a minimum compressive strength of 586 kPa (85 psi). 4.2.1 Radiological Concentration Category 3 waste can be disposed of only if the waste meets one of the following conditions of waste form stability • Stabilization in concrete or other stabilization agents. The stabilized waste must meet the leach index and compression strength criteria of the U.S. Nuclear Regulatory Commission (NRC) *Technical Position on Waste Form*, Section C.2 and Appendix A (NRC 1991).	Compressive strength data including radiation effects, water immersion, thermal cycling, biodegradation

Table B.1. (contd)

Property	Requirement	Basis	IDF Waste Acceptance Criteria[a]	Data Package Content
1.2.2.18 Compression Testing	Each fully loaded package shall be able to withstand a compression load of 50,000 kg. Compliance with this specification shall be established by using the compression test described in 49 CFR 173.465(d). The integrity of the package shall be demonstrated by showing that the dimensions of the tested packages are within the tolerance range and by showing that the seal remains intact in accordance with Specification for *Closure and Sealing*	Stacking in disposal trench.		Waste package design. Not a factor in waste form selection.
1.2.2.19 Manifesting	A shipping manifest shall be prepared for delivery with each shipment of SSW product. Information on the manifest shall satisfy the requirements in DOE Manual 435.1-1, Chapter N, Section I.(2), and NUREG/BR-0204. Any package containing dangerous waste must be labeled and manifested in accordance with WAC 173-303-370 and the *Dangerous Waste Portion of the Resource Conservation and Recovery Act Permit for the Treatment, Storage, and Disposal of Dangerous Wastes* (Permit No. WA 7890008967).	Equivalent to WTP glass packaging requirements	2.5 Waste Receipt and Acceptance Each waste shipment must be accompanied by the following paperwork: • A receipt report • A Uniform Hazardous Waste Manifest • A Land Disposal Restriction Notification/Certification Form (waste subject to 40 CFR Part 268).	Not a factor in waste form selection

Table B.1. (contd)

Property	Requirement	Basis	IDF Waste Acceptance Criteria[(a)]	Data Package Content
1.2.2.20 Waste Form Testing - Leachability Index	The waste form shall have a sodium leachability index greater than 6.0 when tested for 90 days in deionized water using the ANSI/ANS-16.1 procedure. In addition, leachability index performance targets have been established for key radionuclides of concern – iodine and technetium. An iodine-129 leachability index greater than 11.0 and a technetium-99 leachability index greater than 9.0 are desired.	10 CFR Part 61 and NRC Waste Form Technical Position. Performance targets were established based on preliminary risk and performance assessment estimates of groundwater impacts from immobilized LAW and SSW in an Integrated Disposal Facility. The goal is to achieve long-term release performance from SSW that meets or exceeds regulatory requirements based on site-specific risk assessment calculations. Note: ANSI/ANS 16.1 procedure and corresponding leachability indices is based on the assumption of a diffusion-limited release mechanism, which may not apply to radionuclides of concern in the specific waste form selected. However, the diffusion-based LI performance targets provide a standard test and reference point for comparison and evaluation. These leachability indices correspond to fractional releases of iodine-129 and technetium-99 of approximately 1×10^{-05} Ci/yr/Ci disposed and 2×10^{-04} Ci/yr/Ci disposed, respectively.	<u>4.2.1 Radiological Concentration</u> Category 3 waste can be disposed of only if the waste meets one of the following conditions of waste form stability. Stabilization in concrete or other stabilization agents. The stabilized waste must meet the leach index and compression strength criteria of the U.S. Nuclear Regulatory Commission (NRC) *Technical Position on Waste Form*, Section C.2 and Appendix A (NRC 1991).	ANSI/ANS 16.1 data. Include DIW data and data on other leachants.

Table B.1. (contd)

Property	Requirement	Basis	IDF Waste Acceptance Criteria[(a)]	Data Package Content
1.2.2.21 Minimize Waste Volume	The total SSW volume shall be minimized within the constraints of the other specification requirements	Disposal costs are minimized as the SSW volume and package count is minimized.		Waste loading and density.

Table B.1. (contd)

Property	Requirement	Basis	IDF Waste Acceptance Criteria[(a)]	Data Package Content
1.2.2.22 Thermal, Radiation, Biodegradation and Immersion Stability	The ILAW product shall be resistant to thermal, radiation, biodegradation, and immersion degradation, as described in NRC *Technical Position on Waste Form*. Resistance to each of these types of degradation shall be established by showing that the mean compressive strength of representative non-radioactive samples shall be equal to or greater than 3.45E06 Pa and not less than 75 percent of the initial compressive strength after subjecting the samples to the following: Thermal Degradation: Thirty thermal cycles between a high of 60°C and a low of -40°C in accordance with the ASTM B553-79 or an equivalent testing method. Radiation Degradation: Exposure to a minimum radiation dose of 1.0E08 rad or to a dose equivalent to the maximum level of exposure expected from self-irradiation during storage, transportation and disposal if this is greater than 1.0E08 rad.	Compliance with 10 CFR Part 61 and NRC Waste Form Technical Position.	4.2.1 Radiological Concentration Category 3 waste can be disposed of only if the waste meets one of the following conditions of waste form stability. Stabilization in concrete or other stabilization agents. The stabilized waste must meet the leach index and compression strength criteria of the U.S. Nuclear Regulatory Commission (NRC) *Technical Position on Waste Form*, Section C.2 and Appendix A (NRC 1991).	Compressive strength data including radiation effects, water immersion, thermal cycling, biodegradation

Table B.1. (contd)

Property	Requirement	Basis	IDF Waste Acceptance Criteria[(a)]	Data Package Content
1.2.2.22 (contd)	<u>Biodegradation</u>: No evidence of culture growth when representative samples are tested in accordance with ASTM G21-96 and ASTM G22-76 (R1996), or equivalent methods <u>Immersion degradation</u>: Immersion for 90 days under the ANSI/ANS-16.1 testing conditions			
1.2.3 Package Handling	The package shall be compatible with crane lifting and movement. The package shall be equipped with lifting and other handling appurtenances designed to allow safe lifting, movement, and stacking of the packages when fully loaded. The package shall maintain its integrity during handling, transportation, and stacking. The package design shall allow for vertical stacking to a total height of 10 meters.	Interface with current disposal system	<u>4.3.4 Handling</u> All packages must be configured for safe unloading by forklift or crane. Packages that must be unloaded by crane shall be equipped with lifting and other appurtenances designed to allow safe lifting, movement, and stacking of the packages when fully loaded. The package shall maintain its integrity during handling, transportation, and the lifting required for disposal in IDF.	Package design. Not expected to impact waste form selection

(a) *Integrated Disposal Facility Waste Acceptance Criteria*, RPP-8402, Rev. 1, February 23, 2005.

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