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Secondary Waste Form Down-Selection Data Package—Fluidized Bed Steam Reforming Waste Form

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Septemeber 2011

Pacific Northwest
NATIONAL LABORATORY

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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/ORP 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. These waste streams will be vitrified, and the resulting waste canisters will be sent to offsite (high-level waste [HLW]) and onsite (immobilized low-activity waste [ILAW]) repositories. 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 Integrated Disposal Facility (IDF).

To support the selection of a waste form for the liquid secondary wastes from WTP, Washington River Protection Solutions (WRPS) has initiated secondary-waste-form testing work at Pacific Northwest National Laboratory (PNNL). In anticipation of a down-selection process for a waste form for the Solidification Treatment Unit to be added to the ETF, 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. This data package developed for the Fluidized Bed Steam Reforming (FBSR) waste form includes information available in the open literature and from reviewed and released data obtained from testing currently underway.

The FBSR waste form is composed of two main components. The wastes are processed in the FBSR to form a granular product. This is the primary waste form. The granular product is then encapsulated in a binder material to form a monolithic form to limit dispersability and to provide some structural integrity for subsidence prevention in the disposal facility. At the Hanford Site, the FBSR process is being evaluated as a supplemental technology for treating and immobilizing Hanford low-activity waste (LAW) radioactive tank waste and for treating secondary wastes from the WTP pretreatment and LAW vitrification processes. The insoluble sodium aluminosilicate mineral form is the preferred FBSR product for the Hanford tank wastes because the solidified wastes will be disposed of in the IDF.

The primary product from the FBSR process is a granular product composed of sodium aluminosilicate minerals. The sodium aluminosilicate FBSR granular product is a multiphase mineral assemblage of Na-Al-Si (NAS) feldspathoid minerals (sodalite, nosean, and nepheline) with cage and ring structures that sequester anions and cations (Jantzen et al. 2007b). Nepheline is the basic sodium aluminosilicate mineral with the formula Na_2O-Al_2O_3-$2SiO_2$. When sulfates are captured within the cage structure, nosean forms with the formula $3Na_2O$-$3Al_2O_3$-$6SiO_2 \cdot Na_2SO_4$. When chlorides are captured within the cage structure, sodalite forms with the formula $3Na_2O$-$3Al_2O_3$-$6SiO_2 \cdot 2NaCl$. Depending on the waste compositions, process additives such as magnetite are added to iron-bearing spinel minerals that sequester Cr and Ni in the waste.

The FBSR process has been demonstrated at a pilot scale with nonradioactive simulants of Hanford Envelope C (AN-107) and Envelope A (saltcake) tank wastes and with a simulant of the LAW melter off-gas submerged-bed-scrubber liquid effluent. The process has also been demonstrated with the Idaho

National Laboratory (INL) sodium bearing waste (SBW). The testing has been conducted with rhenium as a surrogate for technetium. Limited data are available on the behavior of ^{99}Tc, although radioactive testing with a bench-scale steam reformer is currently underway.

Previously, the FBSR waste form was evaluated as a supplemental treatment technology for the Hanford LAW. Extensive characterization work has been conducted on the FBSR granular product, including mineralogy, the Product Consistency Test (PCT), the Pressurized Unsaturated Flow (PUF) test, and the Single-Pass Flow-Through Test (SPFT). Work has been initiated to characterize the retention and release of radionuclides and constituents of concern, but much more work is needed. Only limited work has been conducted to characterize the FBSR waste form as a waste form for Hanford WTP secondary wastes.

A number of different binders including cements and high-aluminum cements, geopolymers, hydroceramic cements, and Ceramicrete have been evaluated at the laboratory scale for encapsulating the FBSR granular product to form a monolithic waste form. A geopolymer was selected for the most recent FBSR waste form characterization but a final decision on the binder material has not been made.

The FBSR granular product encapsulated in a binder to form a monolith waste form will meet waste acceptance criteria for IDF. The FBSR process produces a dry granular material. Any free liquids would be introduced through the encapsulation process, and that process can be controlled to minimize/eliminate free liquids. The FBSR waste form has been shown to pass the Toxicity Characteristic Leaching Procedure (TCLP) required to meet IDF dangerous waste limitations. As with any waste form, if the concentrations of the constituents of concern are too high, the waste form will not pass TCLP. At the expected concentrations in the secondary wastes, the FBSR product will easily pass TCLP. The FBSR waste form monoliths pass the 500-psi compressive strength requirement. Candidate binders include cements, geopolymers, and Ceramicrete.

Using rhenium as a surrogate for technetium, the FBSR waste form in the GEO-7 geopolymer binder has been shown to meet the target diffusivity for technetium for secondary wastes.

Acronyms and Abbreviations

ANS	American Nuclear Society
ANSI	American National Standards Institute
ART	Advanced Remediation Technologies
ASTM	American Society for Testing and Materials (ASTM International)
BET	Brunauer, Emmett, and Teller
BSR	bench-scale steam reformer
BSSR	bench-scale steam reformer
CFR	U.S. Code of Federal Regulations
COC	constituent of concern
CRR	carbon reduction reformer
DE-Ci	dose-equivalent Curie
DI	deionized (water)
DMR	denitration and mineralization reformer
DOE	U.S. Department of Energy
DST	double-shell tank
Ecology	Washington State Department of Ecology
EM	Environmental Management
EMF	electromotive force
EPA	U.S. Environmental Protection Agency
ES	emission spectroscopy
ESTD	Engineering Scale Technology Demonstration
ETF	Effluent Treatment Facility
FBSR	Fluidized Bed Steam Reformer
GAC	granular activated carbon
HEPA	high-efficiency particulate air (filter)
HLW	high-level waste
HTF	high-temperature filter
ID	inner diameter
IDF	Integrated Disposal Facility
ILAW	immobilized low-activity waste
INEEL	Idaho National Engineering and Environmental Laboratory
INL	Idaho National Laboratory
LAW	low-activity waste
LDR	Land Disposal Restrictions
LERF	Liquid Effluent Retention Facility
LI	leachability index

LLW	low-level waste
LRO	long-range order
MCC	Materials Characterization Center
MRO	medium-range order
NAS	Na-Al-Si (sodium aluminosilicate)
ND	not detected
NO_x	nitrates/nitrites
NRC	U.S. Nuclear Regulatory Commission
OGF	off-gas filter
OPC	ordinary Portland cement
ORP	DOE Office of River Protection
PA	performance assessment
PCT	Product Consistency Test
PNNL	Pacific Northwest National Laboratory
PR	product receiver
PSF	product separation filter
PUF	pressurized unsaturated flow
RCRA	*Resource Conservation and Recovery Act of 1976*
REDOX	reduction oxidation
RPP	River Protection Project
SAIC	Science Applications International Corporation
SBS	submerged-bed scrubber
SBW	sodium-bearing waste
SEM	scanning electron microscopy
SPFT	Single-Pass Flow-Through (test)
SRNL	Savannah River National Laboratory
SRO	short-range order
SRS	Savannah River Site
SSV	superficial space velocity
STAR	Science and Technology Applications Research
SW	secondary waste
TCLP	Toxicity Characteristic Leaching Procedure
THOR®	THermal Organic Reduction
TRU	transuranic
TTT	THOR Treatment Technologies, LLC
UHC	underlying hazardous constituent
UTS	Universal Treatment Standard
WAC	waste acceptance criteria, Washington Administrative Code

WESP	wet electrostatic precipitator
WRPS	Washington River Protection Solutions
WTP	Hanford Tank Waste Treatment and Immobilization Plant
WTP-SW	Hanford WTP secondary waste
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 (DOE/ORP 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 bepoured 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 of 1976* (RCRA) permitted, multi-waste treatment and storage unit 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 online 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 solidifying the liquid secondary wastes (Pierce et al. 2010a, b). 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 (TTT 2009) 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 on data obtained from testing currently underway.

1.1 Origin and Disposition of WTP Liquid Secondary Wastes

The WTP includes three major treatment facilities: a pretreatment building, an 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; and a large-volume, LAW stream with most of the sodium and aluminum. From an environmental protection perspective, the largest fractions of the inventory of technetium-99 (^{99}Tc) and iodine-129 (^{129}I) (both long-lived radionuclides) in the tanks 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, and 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.

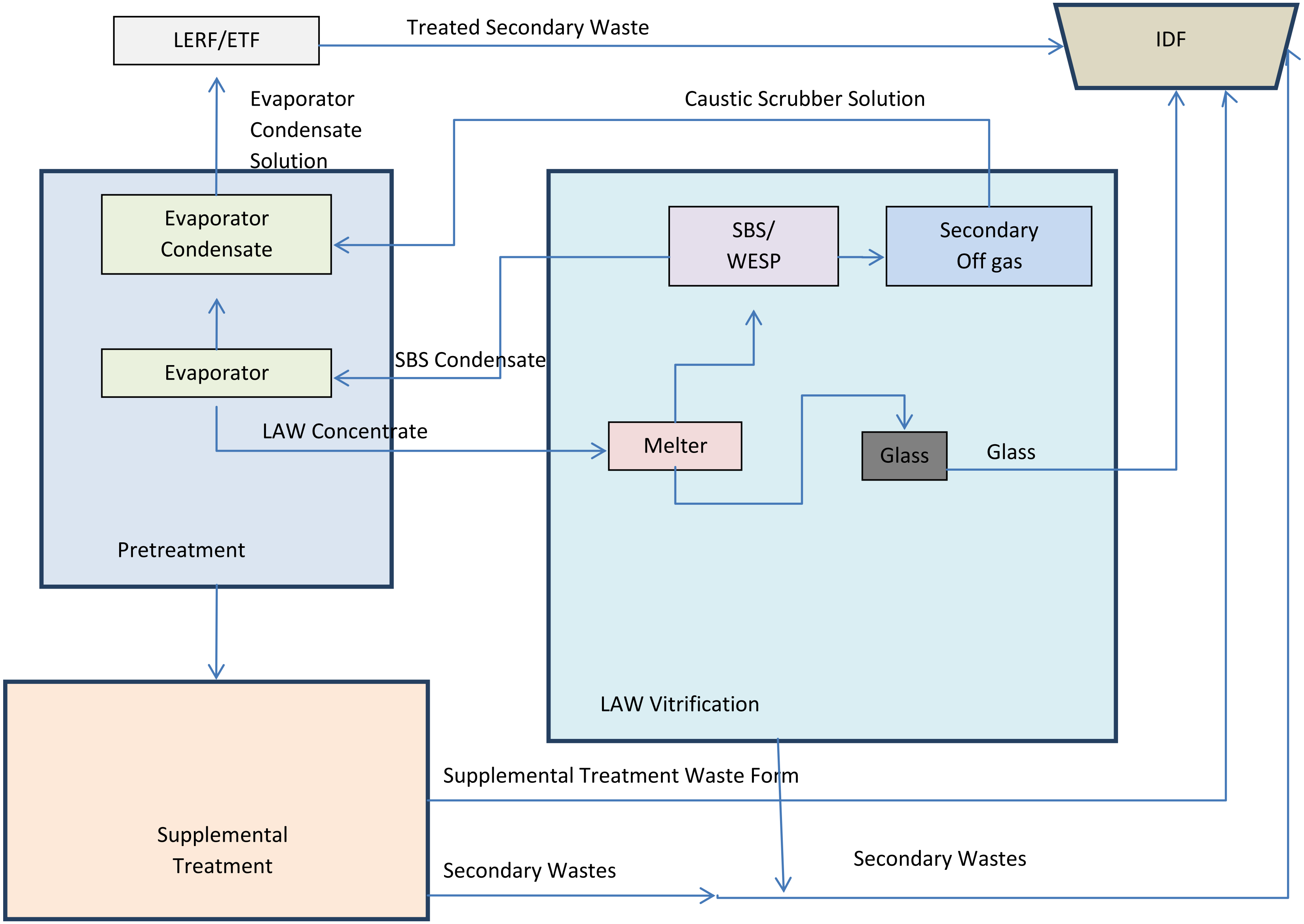


Figure 1.1. Schematic of Secondary Waste Sources

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 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 offgas 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 SBSs and WESPs would go directly to a secondary waste stream exiting the WTP. For example, in an “early LAW” scenario, the LAW melter would begin operations with selected tank wastes before the pretreatment facility came online. 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 (DOE/ORP 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 waste (LLW) and mixed radioactive/hazardous wastes are typically stabilized and solidified before disposal in near-surface facilities. Spence and Shi (2005) provide 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 (<150ºC) 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 for waste forms for the secondary wastes. As part of the Advanced Remediation Technologies (ART) program, THOR Treatment Technologies, LLC (TTT) and Savannah River National Laboratory (SRNL) demonstrated the feasibility of an FBSR 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, DuraLith, Ceramicrete, and FBSR waste forms were identified. In addition, several less-mature technologies, including several aluminosilicates and an iron-oxide mineral called goethite [FeO(OH)] with the capacity to specifically retain technetium, were identified (Pierce et al. 2010a). 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, the following 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

Previous waste form selection processes at the Hanford Site were examined in defining the content to be provided in the waste form down-selection data packages. 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 supplemental waste forms. These are shown in Table 1.1.

Table 1.1. Supplemental Treatment Technology Selection Decision Goals, Criteria, and Measures (Raymond et al. 2004)

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 • Disposal space required • Secondary wastes produced	• Flux at points of undisturbed soil and bottom of the waste packages • Acres of land for disposal site • Potential to emit constituents: solid waste volume, liquid waste volume
Maximize schedule acceleration	• Confidence in meeting 2028 date* • Process robustness	• 50% probability data for achieving 10 GPM throughput • Metric tons of sodium processed by 2028
Maximize cost effectiveness	• Life cycle cost • Peak year cost	• Life cycle 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 the Effluent Treatment Facility capacity • Dose of waste package (impacting handling within disposal system • Volume returned to double-shell tanks (impacting stored waste volume)

*Tri-Party Agreement date for completion of tank waste treatment

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 lists the technical issues, uncertainties, and 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, criteria, and measures developed for the supplemental treatment down-selection and the technical issues/uncertainties and testing objectives recommended for the containerized grout. Appendix A includes expanded Table 1.1 and Table 1.2 with the data package contents to address each measure and testing objective.

Table 1.2. Summary of Testing Recommendations for Containerized Grout Technology—Waste Form Performance (Josephson et al. 2003)

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. *Resource Conservation and Recovery Act of 1976* metals, other radionuclides (e.g., Cs), all listed waste constituents (series of codes for solvents F001-F005), land disposal restrictions 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).

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 (WAC) 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.”

The IDF waste acceptance criteria have not been established for wastes to be disposed of in the facility. There have been several draft waste acceptance criteria proposed, some limited to the ILAW glass waste form and 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 (RPP 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 Part 268 by meeting the universal treatment standards in 40 CFR 268.48 via the Toxicity Characteristic Leaching Procedure (TCLP) test.
- Free Liquids: The waste form shall contain no detectable free liquids as defined in EPA SW-846 Method 9095 (EPA 2004).
- 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 National Standards (ANSI/ANS)-16.1 method (ANS 2008) or EPA draft Method 1315 (EPA 2009c). The waste form shall have a rhenium or technetium LI greater than 9.0. 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 more recent assessments.
- Compressive Strength: The compressive strength of the waste form shall be at least 3.54 E6 Pa (500 psi) when tested in accordance with American Society for Testing and Materials (ASTM) C39/C39M (ASTM 2010c). This is based on the Nuclear Regulatory Commission's *Technical Position on Waste Form* (NRC 1991), which is more restrictive for cement-based waste forms.

1.5 Introduction to the FBSR Data Package

As part of the ART program, DOE chose to demonstrate the capabilities of the THermal Organic Reduction (THOR®) process as a potential means to treat and prepare the Hanford LAW and WTP secondary waste (WTP-SW) for disposal at the IDF (Vora et al. 2009).

The THOR® FBSR process has been shown in previous test programs to effectively convert several types of liquid radioactive waste simulants into solid products (Vora et al. 2009). FBSR is being considered as a potential technology for immobilizing a wide variety of radioactive wastes at the Hanford Site, at the Idaho National Laboratory (INL), and at the Savannah River Site (SRS) (Jantzen et al. 2005b).

Waste liquids may be high in organics, nitrates/nitrites, halides, and/or sulfates (Jantzen et al. 2007b). They include LAW at DOE sites in the United States and other waste streams that may be generated by the advanced nuclear fuel cycle flowsheets that are being considered by the Global Nuclear Energy Partnership (GNEP) initiative (Jantzen et al. 2007b).

The objective of FBSR-related work has been to create geophases (minerals) that would provide leach resistant (durable) waste forms for immobilizing the contaminants that are present in different waste liquids (Olson et al. 2004a). The THOR® FBSR technology converts organic compounds to CO_2 and H_2O and nitrate/nitrite species to N_2, and it produces a solid residue through reactions with superheated steam, the fluidizing medium (Jantzen et al. 2005b).

The FBSR mineral waste form is a granular product but can subsequently be made into a monolith for disposal if necessary (Jantzen et al. 2007b). The mineral components of the waste form are primarily Na-Al-Si (sodium aluminosilicate) (NAS) feldspathoid minerals with cage-like and ring structures and iron-bearing spinel minerals (Jantzen et al. 2005b). The cage and ring structured minerals atomically bond radionuclides like ^{99}Tc and ^{137}Cs and anions such as SO_4, I, F, and Cl (Jantzen et al. 2005b). The spinel minerals appear to stabilize RCRA hazardous species such as Cr and Ni (Jantzen et al. 2005b).

Numerous pilot plant and engineering-scale FBSR demonstrations and tests have been conducted over the last several years that have shown the THOR® process technology capable of processing high-nitrate liquid waste simulants into a solid waste form (Olson et al. 2004a; Vora et al. 2009) as will be presented in the following sections of this data package.

1.6 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 FBSR waste form.

The approach to compiling the information in this report (data package) included:

1. Initially, available literature publications were reviewed to gather the necessary materials and information needed to write the section of the data package provided in the outline.
2. Then each section of the report was composed and written. In some instances, text, tables, and figures from different reference sources were used in this data package to present important information that might be helpful during the decision-making stage and the waste-form down-selection process. This information was also used as a starting point to further discuss important issues and trends observed in the literature related to the use of the FBSR materials as waste forms.

This report contains quoted material from selected references, and within these quotations are many reference callouts. Some of the references called out in the quotations are included in the reference list in this report, but others are not included. To avoid confusion, the reference callouts in the quoted material that are not included in the reference list of this report have been deleted.

2.0 Waste Form Description

The FBSR waste form is composed of two main components. The wastes are processed in the FBSR to form a granular product. This is the primary waste form. The granular product is then encapsulated in a binder material to form a monolithic form to limit dispersability and to provide some structural integrity for subsidence prevention in the disposal facility. The FBSR process has been used to convert simulated liquid radioactive wastes into either a water-soluble carbonate matrix material or an insoluble sodium aluminosilicate material. The sodium aluminosilicate minerals form when clay is added to the FBSR. When no clay is added to the FBSR, the carbonate forms due to the high CO-CO_2 from coal present in the reactor. The carbonate form has been selected for treating INL sodium-bearing waste (SBW) (Landman et al. 2007). The resulting FBSR granular product will be stored for future disposition. At the Savannah River site, plans are to run Tank 48H wastes through an FBSR to form a carbonate solid that will eventually be converted to a glass waste form in the Defense Waste Processing Facility for disposal.

At the Hanford Site, the FBSR process is being evaluated as a supplemental technology for treating and immobilizing Hanford LAW radioactive tank waste and for treating secondary wastes from the WTP pretreatment and LAW vitrification processes. The insoluble sodium aluminosilicate FBSR product is the preferred form for the Hanford tank wastes because the solidified wastes will be disposed of in the IDF. The discussions that follow will focus on the sodium aluminosilicate FBSR waste form. Before a decision was made to convert the INL SBW to a carbonate form, a sodium aluminosilicate form was evaluated. Relevant information on the FBSR SBW product is included.
The FBSR waste form data presented in the following sections are derived from a number of pilot-scale FBSR tests conducted with INL SBW and Hanford LAW and secondary waste simulants.

Table 2.1 summarizes these tests.

2.1 Sodium Aluminosilicate Primary Waste Form

The primary product from the FBSR process is a granular product composed of sodium aluminosilicate minerals. The sodium aluminosilicate FBSR granular product is a multiphase mineral assemblage of NAS feldspathoid minerals (sodalite, nosean, and nepheline) with cage and ring structures that sequester anions and cations (Jantzen et al. 2007b). Nepheline is the basic sodium aluminosilicate mineral with the formula Na_2O-Al_2O_3-$2SiO_2$. When sulfates are captured within the cage structure, nosean forms with the formula $3Na_2O$-$3Al_2O_3$-$6SiO_2{\cdot}Na_2SO_4$. When chlorides are captured within the cage structure, sodalite forms with the formula $3Na_2O$-$3Al_2O_3$-$6SiO_2{\cdot}2NaCl$. Depending on the waste compositions, process additives such as magnetite are added to tie up Cr as $FeCr_2O_4$ (Jantzen et al. 2007b).

Table 2.1. Summary of FBSR Pilot-Scale Sodium Aluminosilicate Waste Form Preparation Tests

Waste	Pilot-Scale Facility	Date	Sample ID	Monolith	Reference
Hanford Wastes					
LAW AN-107, Envelope C	Hazen Research Facility, 6-inch FBSR	December 2001	SCT02-098-FM, PR-01	No	Jantzen (2002); Pareizs et al. (2005)
LAW Saltcake blend	SAIC STAR, 6-inch FBSR	August 2004	BED 1103, Bed 1102, Fines 1125	Blend	Olson et al. (2004a)
LAW Saltcake blend	Hazen Research Facility, 15-inch FBSR	2008	P1 PR bed, HTF fines	Yes	TTT (2009)
WTP-SW LAW melter off-gas recycle	Hazen Research Facility, 15-inch FBSR	2008	P2 PR bed, HTF fines	Yes	TTT (2009)
LAW Saltcake blend	SRNL BSR	2010	---	No	Jantzen et al. (2011)
WTP-SW LAW melter off-gas recycle	SRNL BSR	2010	---	No	Jantzen et al. (2011)
Idaho Wastes					
SBW	SAIC STAR, 6-inch FBSR	July 2003	Bed 260, Bed 272, Bed 277	Blend	Marshall et al. (2003)
SBW	SAIC STAR, 6-inch FBSR	2004	Bed 1173	Blend	Olson et al. (2004b)
SBW	Hazen Research Facility, 15-inch FBSR	2006	DMR4xxx, HTF4xxx	No	Ryan et al. (2008)

Jantzen et al. (2005a) describes the retention of anions and cations within the mineral structures of the sodalite, nosean, and nepheline phases. Probably the most comprehensive discussion on this topic is presented by Jantzen (2008). Sections taken from this reference are provided below:

> *Sodalite minerals are known to accommodate Be in place of Al and* S_2 *in the cage structure, along with Fe, Mn, and Zn, e.g. helvite (*$Mn_4[Be_3Si_3O_{12}]S$*), danalite (*$Fe_4[Be_3Si_3O_{12}]S$*), and genthelvite (*$Zn_4[Be_3Si_3O_{12}]S$*) (Deer et al, 1963). These cage-structured sodalites are also found to retain Mo, Cs, and Sr, B, Ge, I and Br (Deer et al. 1963; Buhl et al. 1989; Fleet 1989). Regardless of the oxidation state of sulfur during processing, the feldspathoid minerals can accommodate sulfur as either sulfate or sulfide.*
>
> *Although neither Cs nor Rb sodalites have been identified as phase pure end members, but Cs and Rb are tolerated in the sodalite structure (Deer et al, 1963; Deer et al. 2004). In addition, Zeolite-A structures are known to form from reaction of CsOH and RbOH with kaolin clay as discussed above (Barrer et al. 1968).*

Further:

> *The flexibility of the sodalite structure … demonstrates that monovalent species such as* Cs^+*,* K^+*,* $Ca_{0.5}$*,* $Sr_{0.5}$*, etc. can substitute for Na+ in the sodalite family of structures, while* $(SO_4)^{-2}$*,* $(MoO_4)^{-2}$*,* $(AsO_4)^{-2}$*,* $(MnO_4)^{-1}$*, and* $(ReO_4)^{-1}$ *[and presumably* $(TcO_4)^{-1}$*], can all substitute for the Cl atoms in the sodalite structure … . For elements such as S, Mo, Re (Tc) and Mn the oxygens in tetrahedral polyhedra around these elements provide the oxygen bonds for the tetrahedral XO4 groups. These oxygen come from four of the six tetrahedra forming a ring along the body diagonal of the cubic unit cell (Hassan and Gruncy 1984). In addition,* I^-*,* Br^-*,* OH^-*, and* NO_3^{-2} *can all substitute for the* Cl^- *atoms in the sodalite structure. Boron and beryllium can substitute for Al in a tetrahedral polyhedra in the sodalite structures as can titanium while elements like iron and zinc substitute for* Na^+ *(Hassan and Gruncy 1984; Deer et al. 2004).*
>
> *All bonding in the sodalite/nosean single unit cell … is ionic and the atoms are regularly arranged. This is similar to the manner of ionic bonding in glass, but more highly ordered than the atomic arrangements in glass... .*
>
> *… the ring structures in nepheline are similar to the ring structures in the sodalites that define the cage structures in the sodalites and Zeolite-A. Nepheline can be a host mineral for other alkali or alkaline earth elements (Cs, K,* $Ca_{0.5}$*) substituting for* Na_+*, while rare earth elements substitute for* Al_3^+ *(Deer et al. 2004). Iron,* Ti_3^+*, Mn, Mg, Ba, Li, Rb, Sr, Zr, Ga, Cu, V, and Yb all substitute in trace amounts in the nepheline lattice (Deer et al. 2004). In addition,* $BaAl_2O_4$*,* $SrAl_2O_4$*,* $(Sr,Ba)Al_2O_4$*,* $RbAlSiO_4$*,* $CsAlSiO_4$*, and* $KFeSiO_4$ *all have nepheline/kalsilite structures with similar ring structures (Deer et al. 2004).*

And:

> *Nepheline is a hexagonal structured feldspathoid mineral. The ring structured aluminosilicate framework of nepheline forms cavities within the framework. There are eight large coordination sites that bond Ca, K, and Cs ionically to nine framework (Al,Si tetrahedral) oxygens and six smaller coordination sites that bond Na ionically to eight framework (Al,Si tetrahedral) oxygens (Deer et al. 1963). The larger nine-fold sites can hold large cations such as Cs, K, and Ca while the smaller sites accommodate the Na. The K nepheline is known as kalsilite ($KAlSiO_4$). In nature, the nepheline structure is known to accommodate Fe, Ti and Mg as well.[50] In addition, rare earth nephelines are known, e.g. $NaYSiO_4$, $Ca_{0.5}YSiO_4$, $NaLaSiO_4$, $KLaSiO_4$, $NaNdSiO_4$, $KNdSiO_4$, and $Ca_{0.5}NdSiO_4$, where the rare earth substitutes for Al in the structure (Barrer 1982). A sodium rich cubic structured nepheline with excess Na is also known, e.g. $(Na_2O)_{0.33}Na[AlSiO_4]$ and was found in the AN-107 FBSR mineralized product. This nepheline structure has large cage like voids in the structure where the Na can bond ionically to 12 framework oxygens (Klingenberg and Felsche, 1986). This cage structured nepheline is not known to occur in nature, but the large cage-like voids should be capable of retaining large radionuclides, especially monovalent radionuclides such as Cs. Likewise, Na_2O deficient nepheline structures are known that have been found in other FBSR mineralizing campaigns for INL's alumina rich Sodium Bearing Waste (SBW).*

Magnetite is sometimes added to the FBSR to sequester Cr in the waste. In this situation and potentially for waste streams rich in iron, spinels form that also retain cations such as Cr within the structure as $FeCr_2O_4$. Jantzen (2008) explains:

> *The spinels such as Fe_3O_4 ($Fe^{+2}Fe_2^{+3} + O_4$) are known to take Cr^{+3} and Ti^{+3} into their lattice in place of Fe^{+3}, and many of the divalent transition metals like Ni^{+2}, Mn^{+2}, Zn^{+2}, Mg^{+2} into their lattice as well (Deer et al. 1962). Spinels have both tetrahedral and octahedral coordination spheres with oxygen. The trivalent ions reside in the four-fold coordination positions and the divalent ions reside in the six-fold coordination positions. All the trivalent and divalent ions are ionically bonded to oxygen.*

The FBSR granular product is composed of two fractions from the FBSR process. Solids collected from the bottom of the fluidized bed are captured in the product receiver (PR). Figure 2.1 shows a photograph of the PR material from the 2008 Hazen pilot-scale test with the Hanford LAW simulant. The PR material includes residual carbon from coal or wood products used in the FBSR as an energy source and as a reductant. The PR material may also include residual alumina used as an initial seed material when the FBSR is first started up. Solids leaving the FBSR entrained in the fluidizing gases are captured in the high-temperature filter. These are a finer particle as shown in Figure 2.2.

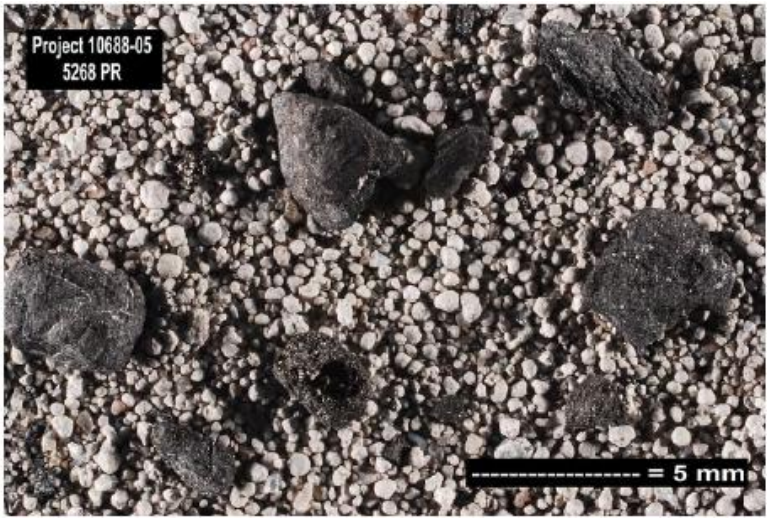


Figure 2.1. Example of FBSR Granular Product from the Product Receiver (from TTT 2009)

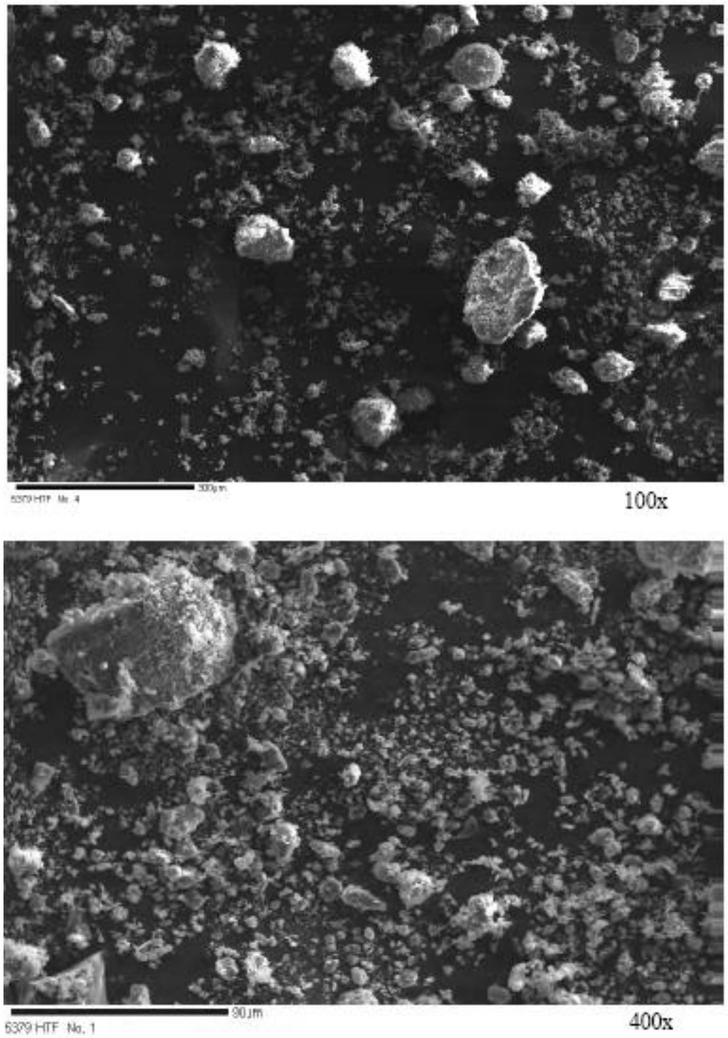


Figure 2.2. Microprobe Photographs of High Temperature Filter (HTF) Fines (from TTT 2009)

Some scanning electron microscopy (SEM) micrographs of the FBSR material from the 2001 Hazen Research facility test with Hanford LAW are presented in Figure 2.3.

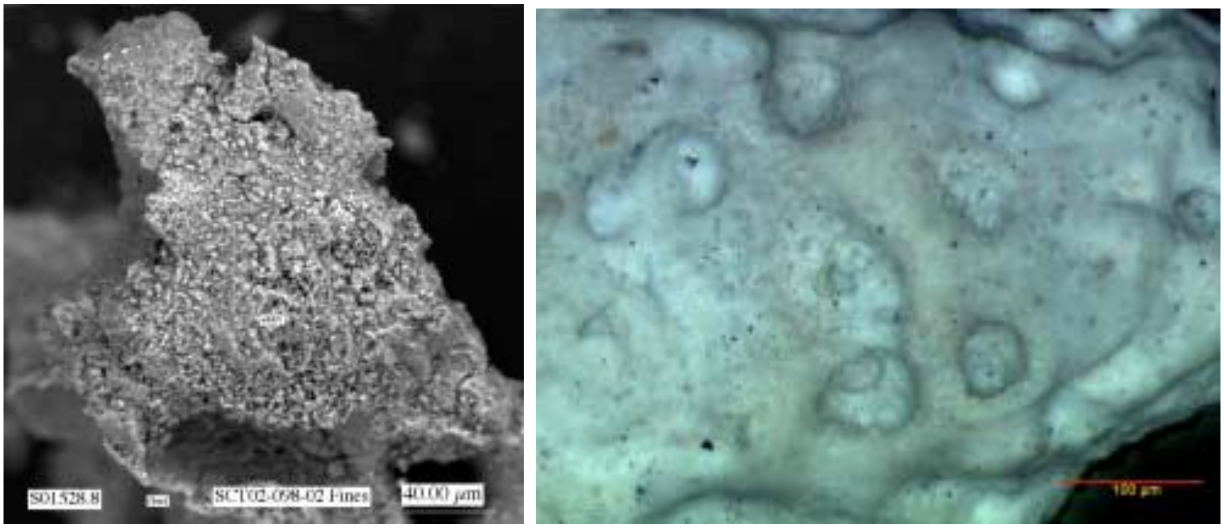
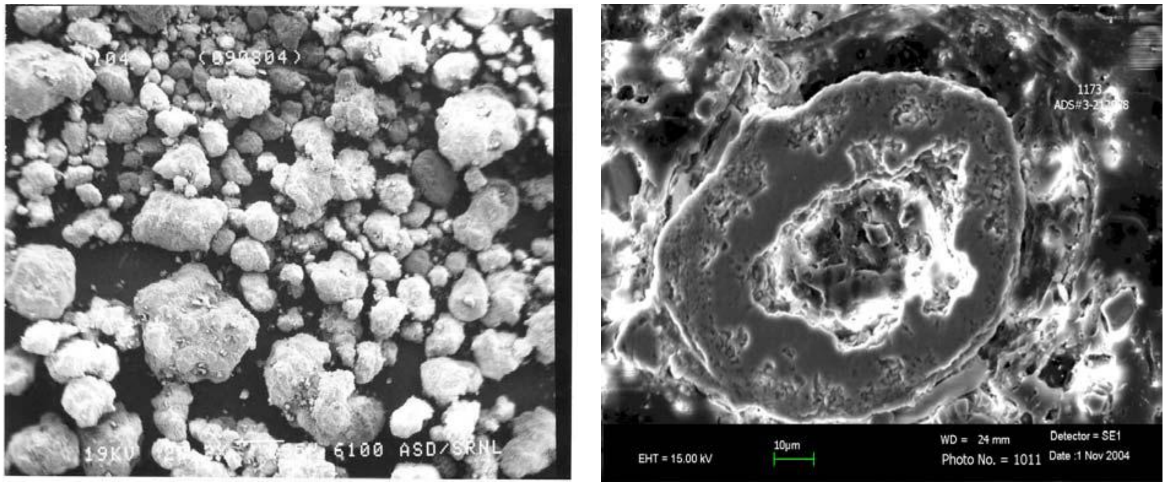


Figure 2.3. SEM Micrographs of Typical FBSR Product Grain (left). Optical photograph of a particle from sample SCT02-098 (FBSR material); the black particles are magnetite (Fe_3O_4) (McGrail et al. 2003c).

The FBSR materials are clearly shown to be porous materials as is evident in the left micrograph of Figure 2.3. It is also worth noticing the presence of magnetite (Fe_3O_4) in this FBSR product. Magnetite contains both Fe(II) and Fe(III) in the crystal structure and therefore may be involved in reactions with redox-sensitive contaminants that may be present in the liquid waste. Iron oxides are also good hosts for contaminants, e.g. forming spinels with Cr and Ni in the wastes.

Figure 2.4a and Figure 2.4b show SEM micrographs by Lorier et al. (2005) of FBSR materials from tests in 2004 with Hanford LAW saltcake simulant and INL SBW, respectively. The image of LAW saltcake FBSR product shows the irregular shape of the granular product. The SBW micrograph shows the internal porosity of a granule in cross-section.

In another study, SEM images of the FBSR material indicated again the presence of substantial porosity in these materials (Pierce 2007) (Figure 2.5).



A. LAW 1123 B. SBW 1173 (sectioned)

Figure 2.4. SEM Photomicrographs of FBSR Bed Product Showing the Surface Topography and Porosity (Lorier et al. 2005)

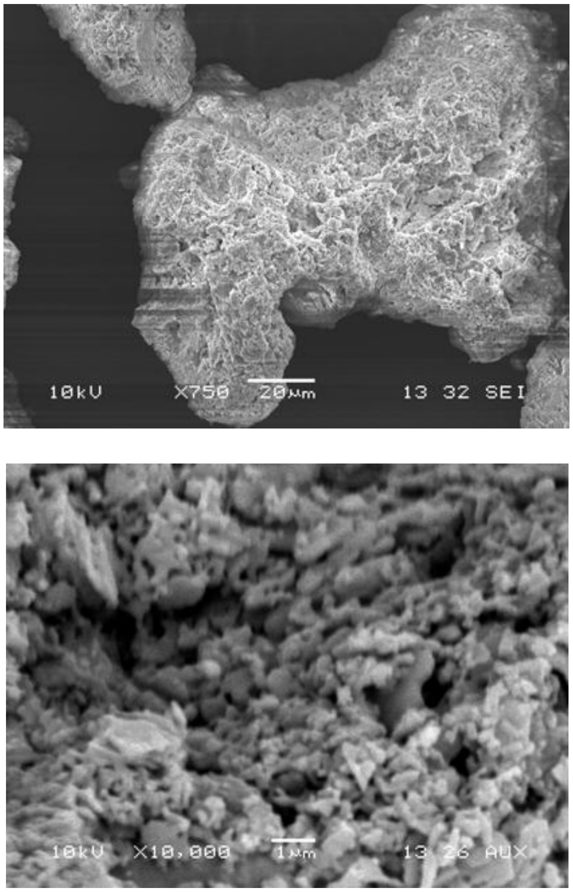


Figure 2.5. SEM Images of FBSR 1123 Product (Pierce 2007)

2.2 Chemical Composition

The chemical composition of the FBSR materials was determined in recent studies conducted over the last decade at SRNL, Idaho National Engineering and Environmental Laboratory (INEEL), and PNNL. Some examples taken from the available literature are presented below with the purpose of presenting the type of chemical elements and the range of concentrations that are present in the FBSR materials.

Elemental and anion compositions of the steam reforming materials (Science and Technology Applications Research [STAR] FBSR bed products and fines) were measured in a study by Jantzen and collaborators (Jantzen et al. 2005b). In this study, the carbon was removed by heating the samples to 525 °C overnight. According to the authors, this temperature is high enough to oxidize (remove) the carbon in the presence of air, but not high enough to change the composition or the phase assemblages as verified by X-ray diffraction (XRD) conducted in the pre- and post-treatment materials. The authors also state that this is the temperature specified in a U.S. Geological Survey (USGS) procedure for carbon removal in preparation for analyzing coal combustion by-products (Bullock et al. 2002).

In this study (Jantzen et al. 2005b), the solid samples were digested with a lithium tetraborate fusion at 1000 °C followed by a hydrochloric acid uptake, and the resulting solutions were analyzed with inductively coupled plasma emission spectroscopy (ICP-ES) for Al, Ca, Cd, Cr, Cs, Cu, Fe, I , K, La, Mg, Mn, Na, Ni, P, Pb, S, Si, and Ti and inductively coupled plasma mass spectroscopy (ICP-MS) for Cs, La, Re, and I. The elemental analyses were done both on a carbon-free basis and with carbon and were compared by mathematically removing the carbon fraction from the analyses performed with the carbon in the product. The anion content was determined from a sodium peroxide/sodium hydroxide fusion at 600 °C, dissolved in water, and analyzed with ion chromatography (IC) for NO_3^-, F^-, and Cl^-. The Fe(II) content was also determined. However, the authors recognized the fact that heating samples to remove the carbon likely might have oxidized the sample and changed the Fe(II)/Fe total ratio. Therefore, the reduction-oxidation (REDOX) was measured on a sample with carbon such that the REDOX was representative of the sample. They reported the results on a carbon-free basis.

The measured cation and anion compositions of the STAR FBSR bed products and fines are given in Table 2.2 (Jantzen et al. 2005b). The elemental analyses were converted by these authors to an oxide and/or a mineral basis for mass balance purposes because the FBSR waste plus co-reactants are all converted to oxides, halides (chlorides, fluorides, iodides), and sulfate minerals during processing. During conversion, the measured REDOX ratios given in Table 2.2 were used to distribute elemental Fe mass to FeO and Fe_2O_3. The authors also determined the amount of Cr present as Cr^{n+} (n is chromium in a mixed oxidation state of +3, +4, +5) vs. Cr^{6+} using an electromotive force (EMF) series method. The measured REDOX given in Table 2.2, when coupled with the EMF series, indicated that 86% of the Cr in the STAR SBW 2003 FBSR product was Cr^{n+}, 78% of the Cr in the STAR LAW 2004 FBSR product was Cr^{n+}, and ~91% of the Cr in the STAR 2004 SBW FBSR product was Cr^{n+}.

These results were comparable to previous results collected from measurements conducted on the Hazen 2002 FBSR material (about 62% of the Cr in the Hazen 2002 FBSR product was Cr^{n+} based on the previously measured REDOX ratio). The mineral mass balances presented in this study (Jantzen et al. 2005b), showed that the 2003 and 2004 SBW FBSR products had Al_2O_3 from the Al_2O_3 starting bed.

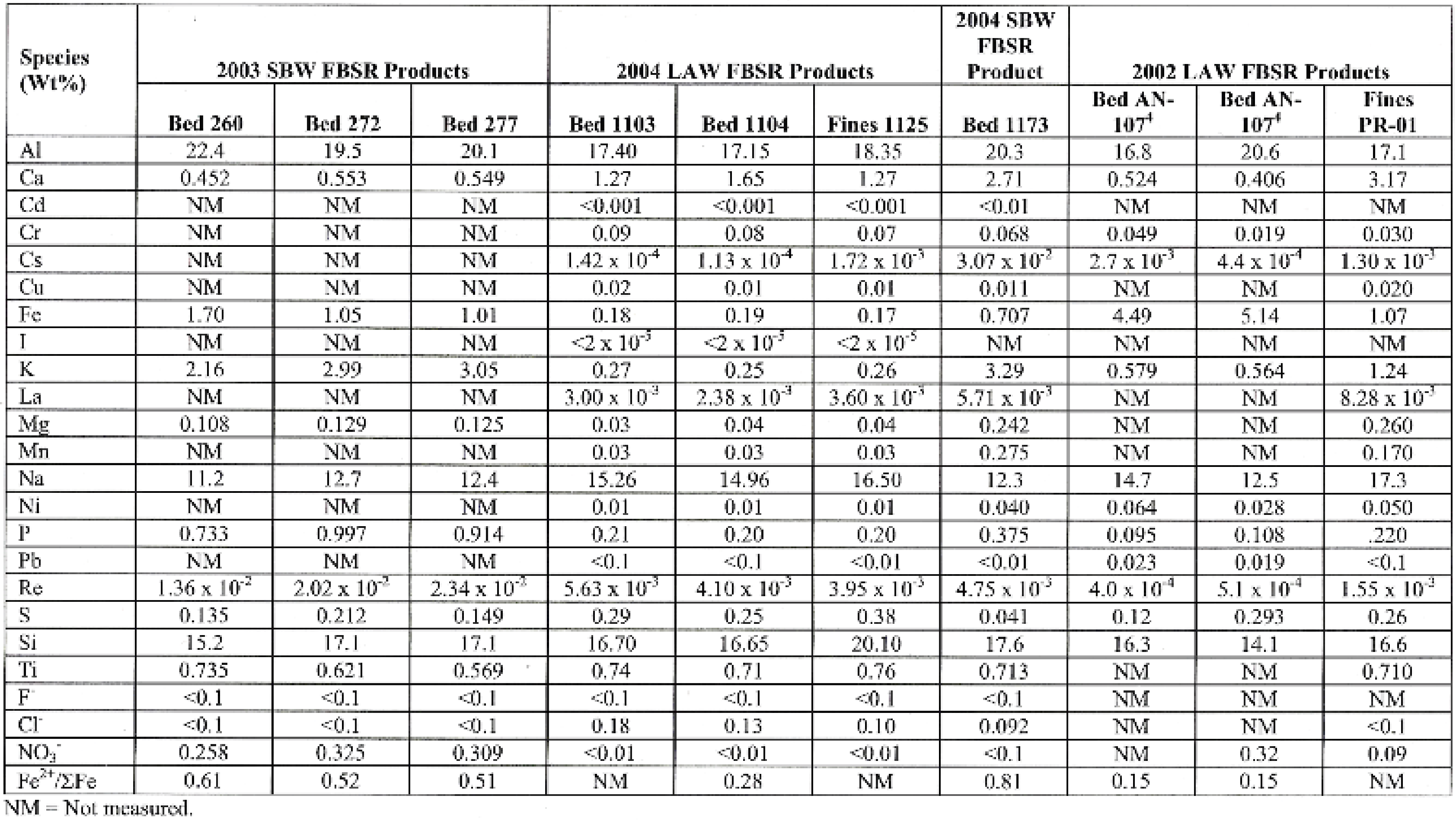
This prediction is consistent with the bed turnovers and with the identification of excess Al_2O_3 in samples from Bed 260 and Bed 1173, confirmed with powder XRD analyses.

Results from the chemical analysis of the FBSR product conducted at PNNL are shown in Table 2.3 (McGrail et al. 2003c). The results presented in this study agreed, in general, with the previous analyses of Jantzen (2002), which are provided in Table 2.3 for reference (McGrail et al. 2003c). Similar tables were provided in another publication by the same first author (McGrail et al. 2003b).

The chemical compositions of additional FBSR materials are also presented in the following publications: Pareizs et al. (2005) and Pierce (2007) (Reproduced here as Table 2.4 and Table 2.5, respectively).

Table 2.6 gives the chemical composition of FBSR granular product from the 2008 Hazen Research facility tests with Hanford LAW saltcake and WTP-SW waste simulants (Vora et al. 2009; TTT 2009). Compositions are provided for the materials collected in the off-gas filter (OGF), high-temperature filter (HTF), and PR. These are average compositions after 95% conversion of the FBSR startup bed to the product bed.

Table 2.2. Elemental and Anion Content of Steam Reformer Bed and Fines (Jantzen et al. 2005a)



Species (Wt%)	2003 SBW FBSR Products			2004 LAW FBSR Products			2004 SBW FBSR Product	2002 LAW FBSR Products		
	Bed 260	Bed 272	Bed 277	Bed 1103	Bed 1104	Fines 1125	Bed 1173	Bed AN-107[4]	Bed AN-107[4]	Fines PR-01
Al	22.4	19.5	20.1	17.40	17.15	18.35	20.3	16.8	20.6	17.1
Ca	0.452	0.553	0.549	1.27	1.65	1.27	2.71	0.524	0.406	3.17
Cd	NM	NM	NM	<0.001	<0.001	<0.001	<0.01	NM	NM	NM
Cr	NM	NM	NM	0.09	0.08	0.07	0.068	0.049	0.019	0.030
Cs	NM	NM	NM	1.42×10^{-4}	1.13×10^{-4}	1.72×10^{-3}	3.07×10^{-2}	2.7×10^{-3}	4.4×10^{-4}	1.30×10^{-3}
Cu	NM	NM	NM	0.02	0.01	0.01	0.011	NM	NM	0.020
Fe	1.70	1.05	1.01	0.18	0.19	0.17	0.707	4.49	5.14	1.07
I	NM	NM	NM	$<2 \times 10^{-5}$	$<2 \times 10^{-5}$	$<2 \times 10^{-5}$	NM	NM	NM	NM
K	2.16	2.99	3.05	0.27	0.25	0.26	3.29	0.579	0.564	1.24
La	NM	NM	NM	3.00×10^{-3}	2.38×10^{-3}	3.60×10^{-3}	5.71×10^{-3}	NM	NM	8.28×10^{-3}
Mg	0.108	0.129	0.125	0.03	0.04	0.04	0.242	NM	NM	0.260
Mn	NM	NM	NM	0.03	0.03	0.03	0.275	NM	NM	0.170
Na	11.2	12.7	12.4	15.26	14.96	16.50	12.3	14.7	12.5	17.3
Ni	NM	NM	NM	0.01	0.01	0.01	0.040	0.064	0.028	0.050
P	0.733	0.997	0.914	0.21	0.20	0.20	0.375	0.095	0.108	.220
Pb	NM	NM	NM	<0.1	<0.1	<0.01	<0.01	0.023	0.019	<0.1
Re	1.36×10^{-2}	2.02×10^{-2}	2.34×10^{-2}	5.63×10^{-3}	4.10×10^{-3}	3.95×10^{-3}	4.75×10^{-3}	4.0×10^{-4}	5.1×10^{-4}	1.55×10^{-3}
S	0.135	0.212	0.149	0.29	0.25	0.38	0.041	0.12	0.293	0.26
Si	15.2	17.1	17.1	16.70	16.65	20.10	17.6	16.3	14.1	16.6
Ti	0.735	0.621	0.569	0.74	0.71	0.76	0.713	NM	NM	0.710
F^-	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	NM	NM	NM
Cl^-	<0.1	<0.1	<0.1	0.18	0.13	0.10	0.092	NM	NM	<0.1
NO_3^-	0.258	0.325	0.309	<0.01	<0.01	<0.01	<0.1	NM	0.32	0.09
$Fe^{2+}/\Sigma Fe$	0.61	0.52	0.51	NM	0.28	NM	0.81	0.15	0.15	NM

NM = Not measured.

Table 2.3. Bulk Compositional Analysis (mass %) of FBSR Product SCT02-098 (McGrail et al. 2003c)

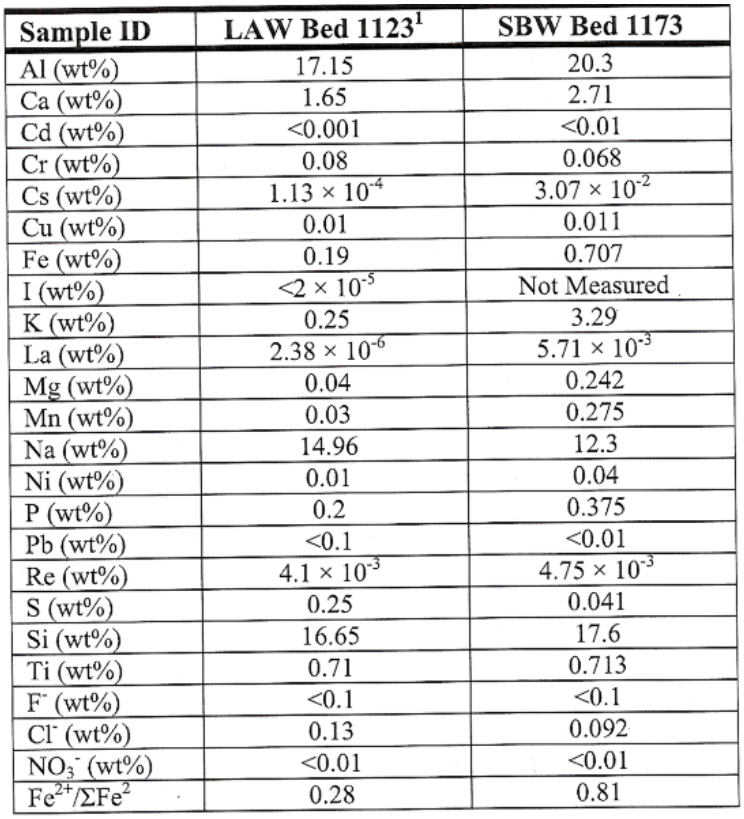
		Fusions		Method	XRF		
Oxide	Jantzen	-10+20	-100+200		-10 +20	-100 +200	Fines
Ag_2O	nr	0.0029	0.0029	MS	BLQ	BLQ	BLQ
Al_2O_3	31.740[a]	39.246	32.133	OES	32.473	29.915	24.992
CaO	0.7332	0.8512	0.7819	OES	0.6651	0.5531	0.7430
Cl	nr	0.2159	0.2159	IC	0.0707	0.0839	0.0994
Cr_2O_3	0.0716	0.0344	0.0461	MS	0.0451	0.0603	0.0395
Cs_2O	0.0029	0.0009	0.0012	MS	0.0323	0.0360	0.0297
F	nr	0.0056	0.0056	IC	BLQ	BLQ	BLQ
Fe_2O_3	5.4471	7.2725	5.0056	OES	7.1382	4.7855	1.9740
FeO	0.8749	nd	nd		nd	nd	nd
K_2O	0.6975	0.7100	0.8400	OES	0.6866	0.7680	0.6746
Li_2O	nr	0.2445	0.2187	MS	BLQ	BLQ	BLQ
MgO	nr	0.1366	0.1326	OES	0.0541	0.0528	0.0480
MnO	nr	0.0743	0.0254	OES	0.0735	0.0263	0.0262
MoO_2	nr	0.0053	0.0050	OES	0.0247	0.0215	0.0379
Na_2O	19.815	16.870	21.227	OES	17.052	18.821	29.660
NiO	0.0814	0.0398	0.0571	MS	0.0440	0.0675	0.0477
P_2O_5	0.2176	0.2499	0.2057	OES	0.2443	0.1850	0.2257
PbO	0.0175	0.0182	0.0182	OES+MS	0.0247	0.0272	0.0647
ReO_2	0.0005	0.0005	0.0007	MS	BLQ	BLQ	BLQ
SiO_2	34.870	29.336	37.526	OES	37.931	42.055	39.039
SO_3	0.9310[b]	0.8107	0.9297	OES	0.6220	0.6819	0.6967
TiO_2	nr	1.6228	1.2617	OES	1.8307	1.4853	1.2626
V_2O_5	nr	0.0685	0.0311	MS	0.0318	0.0140	0.0157
ZnO	nr	0.0184	0.0159	OES+MS	0.0080	0.0086	0.0068
ZrO_2	nr	0.1157	0.0300	OES+MS	0.1250	0.0293	0.0283

BLQ = Below Limit of Quantification; nr = not reported; nd = not determined

[a] Five significant figures are shown to accurately capture the low concentration of ReO_2 in the sample. Mass percents of oxides with concentrations above 0.001% should not be considered accurate to five significant figures.

[b] Converted from SO_4 value reported by Jantzen

Table 2.4. Elemental and Anion Content of Coal-Free Steam Reformer Bed Products (Pareizs et al. 2005)



Sample ID	LAW Bed 1123[1]	SBW Bed 1173
Al (wt%)	17.15	20.3
Ca (wt%)	1.65	2.71
Cd (wt%)	<0.001	<0.01
Cr (wt%)	0.08	0.068
Cs (wt%)	1.13×10^{-4}	3.07×10^{-2}
Cu (wt%)	0.01	0.011
Fe (wt%)	0.19	0.707
I (wt%)	$<2 \times 10^{-5}$	Not Measured
K (wt%)	0.25	3.29
La (wt%)	2.38×10^{-6}	5.71×10^{-3}
Mg (wt%)	0.04	0.242
Mn (wt%)	0.03	0.275
Na (wt%)	14.96	12.3
Ni (wt%)	0.01	0.04
P (wt%)	0.2	0.375
Pb (wt%)	<0.1	<0.01
Re (wt%)	4.1×10^{-3}	4.75×10^{-3}
S (wt%)	0.25	0.041
Si (wt%)	16.65	17.6
Ti (wt%)	0.71	0.713
F^- (wt%)	<0.1	<0.1
Cl^- (wt%)	0.13	0.092
NO_3^- (wt%)	<0.01	<0.01
$Fe^{2+}/\Sigma Fe^{2}$	0.28	0.81

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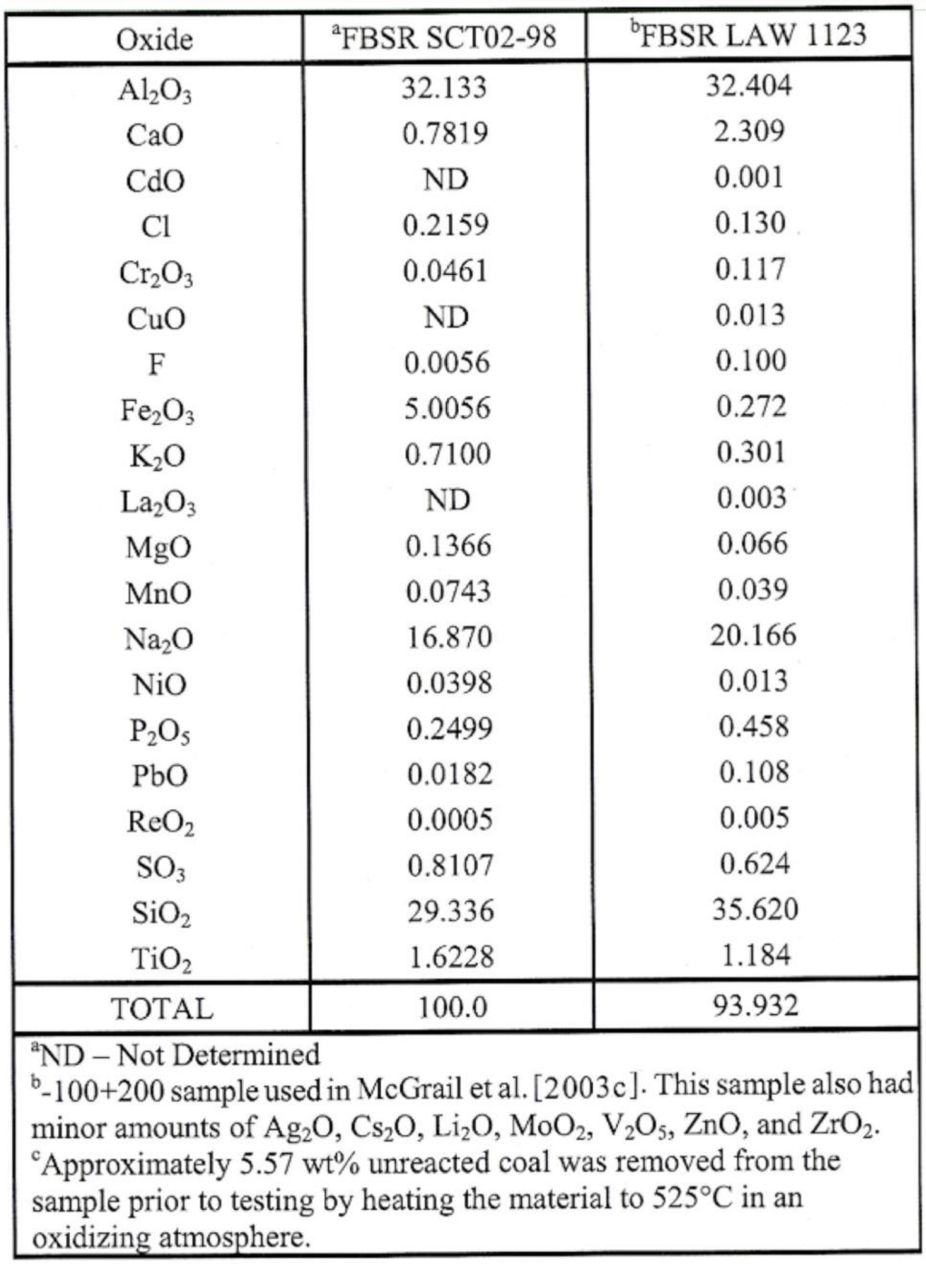
[1] Pareizs et al. (2005) states LAW 1123 as LAW 1104. The LAW 1123 and LAW 1104 products are the same material – bed product after 55 hours of LAW FBSR processing – but subsampled at different times.

[2] The $Fe^{2+}/\Sigma Fe$ ratio was determined on samples where the coal was removed by hand as heating to remove the carbon would have changed the ratio and the measurement did not appear sensitive to the traces of coal remaining.

Table 2.5. Normalized Chemical Composition in Mass % of the FBSR Bed Material, SCT02-98 and LAW 1123 (Pierce 2007)



Oxide	[a]FBSR SCT02-98	[b]FBSR LAW 1123
Al_2O_3	32.133	32.404
CaO	0.7819	2.309
CdO	ND	0.001
Cl	0.2159	0.130
Cr_2O_3	0.0461	0.117
CuO	ND	0.013
F	0.0056	0.100
Fe_2O_3	5.0056	0.272
K_2O	0.7100	0.301
La_2O_3	ND	0.003
MgO	0.1366	0.066
MnO	0.0743	0.039
Na_2O	16.870	20.166
NiO	0.0398	0.013
P_2O_5	0.2499	0.458
PbO	0.0182	0.108
ReO_2	0.0005	0.005
SO_3	0.8107	0.624
SiO_2	29.336	35.620
TiO_2	1.6228	1.184
TOTAL	100.0	93.932

[a] ND – Not Determined

[b] -100+200 sample used in McGrail et al. [2003c]. This sample also had minor amounts of Ag_2O, Cs_2O, Li_2O, MoO_2, V_2O_5, ZnO, and ZrO_2.

[c] Approximately 5.57 wt% unreacted coal was removed from the sample prior to testing by heating the material to 525°C in an oxidizing atmosphere.

Table 2.6. Average Composition (wt%) of FBSR Product From 2008 Hanford LAW and WTP-SW Tests (from Vora et al. 2009)

	Hanford LAW Saltcake			WTP-SW LAW Melter Off-Gas Recycle		
Constituent	OGF	HTF	PR	OGF	HTF	PR
Al	17	17	20	27	18	28
Ag	0.02	0.01	0.03	0.01	0.02	0.02
As	0.01	0.01	0.01	0.01	0.004	0.001
B	0.02	0.28	0.08	0.02	0.13	0.25
Ba	0.00	0.12	0.10	0.00	0.02	0.01
Ca	0.06	0.08	0.07	0.13	0.14	0.05
Cd	0.06	0.04	0.09	0.05	0.03	0.03
Fe	0.5	0.6	5.2	0.4	0.6	4.5
Mg	0.01	0.01	0.02	0.02	0.03	0.03
I	0.09	0.10	0.05	0.05	0.03	0.02
Na	15	12	11	8	10	7
K	0.1	0.1	0.1	0.08	0.2	0.2
Si	19	20	14	9	15	10
Sb	0.07	0.06	0.06	0.03	0.04	0.02
Se	0.002	0.004	0.003	0.03	0.02	0.004
Ti	0.7	0.7	0.6	0.4	0.6	0.4
Tl	0.08	0.03	0.005	0.03	0.09	-
Cs	0.22	0.22	0.08	0.14	0.36	0.12
Cr	0.03	0.04	0.05	0.02	0.04	0.03
Pb	0.12	0.13	0.09	0.10	0.05	0.06
Ni	0.09	0.07	0.08	0.06	0.06	0.04
Zn	0.003	0.05	0.05	0.003	0.04	0.08
Re	0.02	0.02	0.05	0.01	0.02	0.04
Cl	0.17	0.09	0.04	0.18	0.15	0.04
F	0.01	0.09	0.02	0.15	0.47	0.08
NO_3	-	0.004	0.004	-	-	-
NO_2	-	-	-	-	-	-
PO_4	0.7	0.7	0.8	0.4	0.4	0.2
SO_4	0.9	0.5	0.5	0.8	0.4	0.3
CO_3	-	-	0.3	-	-	-
Total Carbon	0.7	7.1	6.8	2.2	14.8	7.6
O (calculated)	42	43	40	37	38	40

2.3 Phase Composition and Mineralogy

Studies have been conducted with different FBSR materials to determine the minerals that are present in these materials. Most of these minerals are believed to belong to the groups of nepheline, sodalite, and carnegieite, all feldspathoids with a one-to-one-to-one molar ratio of Si:Al:Na. Jantzen and Crawford's

(2010) summary of the mineral phases identified in the Hanford LAW and WTP-SW pilot-scale tests and the INL SBW tests is reproduced here as Table 2.7. Nepheline ($NaAlSiO_4$) is the primary phase formed. The fines captured in the HTF have a shorter residence time in the FBSR and contain low-carnegieite. Carnegeite is a metastable form of nepheline with the same chemical composition but with less atomic order. It usually forms due to rapid cooling and readily transforms to nepheline upon heating (Jantzen and Crawford 2010). Nepheline and carnegeite have ring structures.

Nosean ($Na_6[Al_6Si_6O_{24}](Na_2SO_4)$) and sodalite ($Na_6[Al_6Si_6O_{24}](NaCl)_2$) are identified as minor sodium aluminosilicate phases in the FBSR granular product. Nosean and sodalite have cage structures that can retain anions and radionuclides that bond ionically within the structure. Table 2.8 shows how various elements within the tank wastes may substitute in the nepheline, sodalite, and nosean structures (Jantzen et al. 2011).

The oxidation state can affect how and where contaminants are captured in the FBSR product (Jantzen 2008). The FBSR process is run in a reducing environment with a log oxygen fugacity of -20 to -21. Under these conditions, a redox-sensitive species, such as chromium, is predicted to be 50 to 70% reduced to Cr^{3+} and would be sequestered in a spinel (hematite or magnetite) phase. Sulfur is predicted to be only 1 to 19% reduced to S^{2+} and would remain oxidized and enter the sodalite phase as SO_4 in the +4 oxidation state.

Rhenium, a non-radioactive surrogate for technetium, is predicted to be only 2 to 6% reduced to the +4 oxidation state at the nominal operating conditions. At the +7 oxidation state, rhenium, and by association, technetium, are predicted to enter the sodalite phase. Mattigod et al. (2006) were able to synthesize sodalite [$Na_8 (AlSiO_4)_6(ReO_4)_2$] that contained Re(VII). Its crystal structure was determined from Rietveld refinement of experimental XRD data. This study showed that Re(VII) can be incorporated into solids. REDOX control is important for making certain that the contaminants enter the desired FBSR mineral phases. The 2008 Hazen Research facility FBSR tests with Hanford LAW and WTP-SW were conducted under conditions that the HTF product was much more reduced than the PR product (TTT 2009; Jantzen and Crawford 2010).[1] Only 2.5% of the Re was in the +7 state and 1% of the S was in the +4 state in the HTF product, compared to 94 to 95% Re(VII) and 86 to 89% S^{4+} in the PR product.

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[1] Since writing these documents, SRNL has found an interference in the REDOX measurement from “high” coal content (coal content reaches 14–15 wt%). The HTF fines were very coal rich and therefore the fines may not have been more reduced than the bed material because the phase assemblages are the same. (Personal communication from Carol Jantzen).

Table 2.7. Mineral Phases Identified in FBSR Products (from Jantzen and Crawford 2010)

FBSR Product	**Low-Carnegieite** Nominally $NaAlSiO_4$	**Nepheline** Nominally $NaAlSiO_4$ or $K_{0.25}Na_{0.75}AlSiO_4$	**Nosean** $Na_6[Al_6Si_6O_{24}](Na_2SO_4)$ and/or **Sodalite** $Na_6[Al_6Si_6O_{24}](2NaX$ where X=Cl,F,I)	**Other Minor Components**
Hanford Envelope "C" LAW Wastes (2002) $Fe^{+2}/\Sigma Fe$ of Bed = 0.15				
SCT02-098-FM		Major	Minor	Al_2O_3, Fe_2O_3, Fe_3O_4
Fines PR-01	Major	Major	Minor	Al_2O_3, Fe_2O_3, Fe_3O_4
Hanford Envelope "A" LAW Wastes (2004) $Fe^{+2}/\Sigma Fe$ of Bed = 0.28-0.81				
Bed 1103	Major	Major	Minor	TiO_2
Bed 1104	Major	Major	Minor	TiO_2
Fines 1125	Major	Minor		TiO_2
INL SBW Wastes (2003-2004) Fe+2/ΣFe of Bed = 0.51-0.61				
Bed 260	Minor	Major	Trace	Al_2O_3 and TiO_2
Bed 272	Minor	Major	Trace	TiO_2
Bed 277	Minor	Major	Trace	TiO_2
Bed 1173		Major	Trace	Al_2O_3, SiO_2, $NaAl_{11}O_{17}$ and $(Ca,Na)SiO_3$
Hanford Envelope "A" LAW Wastes (2008) $Fe^{+2}/\Sigma Fe$ of Bed = 0.41-0.90				
PR Bed Product 5274 (P1A)	Minor	Minor		Al_2O_3
PR Bed Product 5316 (P1A)	Minor	Minor		Pyrophyllite $(Al_{1.333}Si_{2.667}O_{6.667}(OH)_{1.333})$
HTF Fines 5280 (P1A)	Minor	Minor		$NaAl_{11}O_{17}$, TiO_2
HTF Fines 5297 (P1A)	Minor	Minor	Minor	SiO_2
PR Bed Product 5359 (P1B)	Minor	Minor		Pyrophyllite
PR Bed Product 5372 (P1B)	Minor	Minor		Pyrophyllite
HTF Fines 5351 (P1B)	Minor	Minor		SiO_2
HTF Fines 5357 (P1B)	Minor	Minor		TiO_2
Composite (P1A)	Minor	Minor		SiO_2 and TiO_2
Composite (P1B)	Minor	Minor		SiO_2 and TiO_2
Hanford Melter Off-Gas Recycle (WTP SW) Wastes (2008) $Fe^{+2}/\Sigma Fe$ =0.41-0.90				
PR 5475 (P2A)	Minor	Minor	Minor	Pyrophyllite
HTF Fines 5471 (P2A)	Minor	Minor		SiO_2
PR 5522 (P2B)	Minor	Minor	Minor	Pyrophyllite, TiO_2
HTF Fines 5520 (P2B)	Minor	Minor		SiO_2 and TiO_2
Composite (P2B)	Minor	Minor	Minor	SiO_2

Table 2.8. Cation and Anion Substitution in Feldspathoid Mineral Structures (from Jantzen et al. 2011)

Nepheline—Kalsilite Structures$^{(a)}$	Sodalite Structures$^{(b)}$	Nosean Structures
$Na_xAl_ySi_zO_4^{(c)}$ *where x=1-1.33, y and z = 0.55-1.1*	$Na_6Al_6Si_6O_{24}](NaCl)_2^{(c)}$	$Na_6Al_6Si_6O_{24}](Na_2SO_4)^{(c,d)}$
$KAlSiO_4^{(c)}$	$Na_6Al_6Si_6O_{24}](NaF)_2^{(c)}$	$Na_6Al_6Si_6O_{24}](Na_2MoO_4)^{(c,e)}$
$K_{0.25}Na_{0.75}AlSiO_4^{(c)}$	$Na_6Al_6Si_6O_{24}](NaI)_2^{(d)}$	$[Na_6Al_6Si_6O_{24}]((Ca,Na)SO_4)_{1\text{-}2}^{(f)}$
$(Na_2O)_{0.33}NaAlSiO_4^{(k)}$	$Na_6Al_6Si_6O_{24}](NaBr)_2^{(d)}$	$[(Ca,Na)_6Al_6Si_6O_{24}]((Ca,Na)S,SO_4,Cl)$
$CsAlSiO_4^{(c)}$	$[Na_6Al_6Si_6O_{24}](\ NaReO_4)_2^{(g)}$	
$RbAlSiO_4^{(c)}$	$[Na_6Al_6Si_6O_{24}](NaMnO_4)_2^{(h)}$	
$(Ca_{0.5},Sr_{0.5})AlSiO_4^{(c)}$	$(NaAlSiO_4)_6(NaBO_4)_2^{(i,\ j)}$	
$(Sr,Ba)Al_2O_4^{(c)}$	$Mn_4[Be_3Si_3O_{12}]S^{(d)}$	
$KFeSiO_4^{(c)}$	$Fe_4[Be_3Si_3O_{12}]S^{(d)}$	
$(Na,Ca_{0.5})YSiO_4^{(h)}$	$Zn_4[Be_3Si_3O_{12}]S^{(d)}$	
$(Na,K)LaSiO_4^{(h)}$		
$(Na,K,Ca_{0.5})NdSiO_4^{(h)}$		

(a) Iron, Ti^{3+}, Mn, Mg, Ba, Li, Rb, Sr, Zr, Ga, Cu, V, and Yb all substitute in trace amounts in nepheline (Deer et al. 2004).
(b) Higher valent anionic groups such as AsO_4^{3-} and CrO_4^{2-} form Na_2XO_4 groups in the cage structure where X = Cr, Se, W, P, V, and As (Barrer 1982).
(c) Deer et al. (2004).
(d) Deer et al. (1963).
(e) Brookings (1984).
(f) Dana (1932).
(g) Mattigod et al. (2006).
(h) Barrer (1982).
(i) Buhl et al. (1989).
(j) Tobbens and Buhl (2000).
(k) Klingenberg and Felsche (1986).

In addition to the sodium aluminosilicate phases, other minor phases have been identified using XRD in the FBSR granular product. These include quartz (SiO_2) and anatase (TiO_2), which are impurities in the clays used as mineralizing agents in the FBSR. Corundum (Al_2O_3) is used as the seed material for starting up the FBSR process. Its concentration decreases over time as the starting FBSR bed material leaves through the product receiver. Hematite (Fe_2O_3) and magnetite (Fe_3O_4) were identified in the Hanford AN-107 Envelope A product, most likely because of the iron oxide additive used as a denitration catalyst (Jantzen 2002). Jantzen et al. (2006b) also report that amorphous metakaolin was identified by SEM in the early LAW Envelope C and Envelope A FBSR tests.

2.4 Encapsulating Material (FBSR waste form)

The FBSR granular product will need to be encapsulated in a binder or be contained within high-integrity containers to meet Hanford Integrated Disposal Facility requirements for compressive strength. The compressive strength requirement is driven by the need to prevent subsidence of the disposal facility to maintain the functionality of the surface cap and barriers. Encapsulating the granular product also helps reduce the impact of dispersible materials in intruder scenarios.

There are many materials that can be used to encapsulate the granular FBSR material to make it into a monolith. Several studies have been conducted to evaluate different binder materials for encapsulating the FBSR granular product (Jantzen 2006b; Jantzen 2007; TTT 2009). There are no known studies of pressing and sintering in which attempts have been made to consolidate the FBSR material alone.

Jantzen (2006b, 2007) evaluated cementitous waste form binders based on ordinary Portland cement (OPC), Ceramicrete phosphate-bonded ceramic, and hydroceramic cements. The cement monoliths were prepared with Type II Portland cement and Portland cement plus precipitated silica as a chemically pure representative of a fly ash pozzolanic material. Ceramicrete is a phosphate-based cement developed at Argonne National Laboratory by Wagh and coworkers (Singh et al. 1997, 1998; Wagh et al. 1999a, b). It is made from an acidic solution of potassium dihydrogen phosphate (KH_2PO_4) and MgO. Hydroceramics are prepared through the reaction of a sodium hydroxide solution with metakaolin clay. Under controlled curing conditions, the clay and caustic react to form zeolite mineral phases. All three binders are formed at temperatures less than 100 ºC. Monoliths were prepared from FBSR samples prepared in the Science Applications International Corporation (SAIC) STAR facility in 2003-2004 using Idaho SBW and Hanford LAW simulants. The resulting monoliths were evaluated with respect to LAW glass acceptance criteria, including sodium waste loading to be equivalent to that for glass (>14 wt% Na_2O in waste for LAW Envelope A), compressive strength (>500 psi), and Product Consistency Test (PCT) leachability for Na and Re ($< 2 g/m^2$). Three of the cement formulations and one hydroceramic formulation met the all the performance criteria (see Sections 6 and 7). All but one of the cement and hydroceramic formulations met the compressive strength requirements relevant to secondary wastes.

In a later study (TTT 2009; Jantzen and Crawford 2010), OPC, high-alumina cements, geopolymers, Ceramicrete, and an advanced silicone geopolymer composite material (NuCap™ developed by Global Matrechs, Inc.) were evaluated for encapsulating FBSR granular product from the Hazen Research pilot-scale facility testing with Hanford LAW and secondary-waste simulants in 2008. OPCs consist mainly of calcium silicates. High-alumina cements are composed of calcium aluminates; three formulations were tested. Six geopolymer formulations prepared with kaolin clay and sodium silicate and one geopolymer formulation prepared with fly ash and sodium hydroxide were tested. Evaluation and down-selection of the monolith material was performed with the LAW granular product. After durability and compressive strength testing based on 2-in. cubes, larger 3-in.-diameter × 6-in. and 6-in. × 12-in. cylindrical monoliths were prepared with four of the binder formulations and the LAW and secondary waste FBSR granular product. Based on that testing, 2-in.-diameter × 4-in. cylinders of the geopolymer were prepared with fly ash and sodium hydroxide (GEO-7) and the secondary-waste FBSR granular product for further characterization. There is no chemical composition data or mineralogy data identified in the literature on the FBSR material in the various binder matrices.

2.5 Waste Form Container/Package

The waste form container/package provides both protection and containment for the waste form within during production, transportation, and storage. A waste form container or package has not been selected for the (Cast Stone, DuraLith, Ceramicrete, or FBSR) waste form. The waste form container will need to meet requirements for transporting radioactive and hazardous materials as specified in

49 CFR Part 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 of the following materials acceptable to the IDF:

- metal, concrete, masonry
- fire-retardant-treated or painted wood
- rigid plastic with 25 maximum flame spread rating or coating
- flexible plastic packaging materials with similar 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 affecting the quality of the waste form.

The container will also be configured for ease of filling to maximize the volume of the 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 included for each package.

2.6 Range of Wastes/Compositions Tested

Most of the FBSR sodium aluminosilicate product pilot-scale processing tests have been conducted with INEEL SBW and different compositions of Hanford LAW. One test has also been conducted with a simulant of the SBS liquid effluent for the Hanford WTP LAW melter that is recycled back to the LAW melter in the WTP flowsheet.

Approximately 1 million gallons of radioactive SBW are currently contained in the tank farm at the INL. SBW is the remaining high-activity liquid waste at the Idaho Nuclear Technology and Engineering

Center (INTEC) that must be removed from the underground storage tanks and stabilized into a solid waste form. It was generated from sodium carbonate scrubbing of the tributyl phosphate extractant used in the separations process, from the second and third cycles of the spent nuclear fuel processing, and from decontamination of HLW facilities. It contains a small amount (< 5%) of undissolved solids. It is highly acidic (> 2 M acid) and relatively high in sodium and potassium content from the solutions used for decontamination. SBW is high in TRUs and is best characterized as mixed TRU waste. The SBW simulant used in the FBSR testing is based on the wastes in Tank WM-180 at INL. Table 2.9 shows the composition of the SBW simulant used in the 2003 pilot-scale test at the STAR facility in Idaho (Soelberg et al. 2004). The 2006 SBW test using the Engineering Scale Technology Demonstration (ESTD) at the Hazen Research facility used a SBW simulant based on worst-case concentrations based on actual waste analyses and included surrogates for undissolved solids in some of the testing (Ryan et al. 2008).

Table 2.9. Composition of SBW Simulant used in 2003 STAR Pilot-Scale Test (from Soelberg et al. 2004)

Component	Molarity	Concentration, g/L
Acid	1.1	1.1
Aluminum	0.66	18
Boron	0.012	0.13
Calcium	0.0472	1.9
Cesium	0.0032	0.43
Chromium	0.0033	0.17
Copper	0.00070	0.044
Iron	0.022	1.2
Lead	0.0013	0.27
Magnesium	0.012	0.29
Manganese	0.014	0.77
Mercury	0.0014	0.27
Nickel	0.0015	0.086
Potassium	0.20	7.7
Rhenium	0.0011	0.20
Silicon	-	-
Sodium	2.1	47
Zinc	0.0011	0.069
Chloride	0.030	1.1
Fluoride	0.024	0.45
Nitrate	5.3	330
Phosphate	0.029	2.7
Sulfate	0.070	6.7
Water		838
Density		**1.259**

Four pilot-scale tests have been conducted with various Hanford waste simulants. A test in 2001 using the Hazen Research test facility used a simulant based on Tank AN-107, an Envelope C waste

(Jantzen et al. 2006b). The 2004 FBSR test at the STAR facility used a Hanford saltcake simulant based on the work of Rassat et al. (2003) and Olson et al. (2004a). This simulant represents a blend of 68 saltcake tanks; the composition is shown in Table 2.10. In 2008, additional pilot-scale tests were conducted at the Hazen Research test facility with the Hanford saltcake simulant for LAW and a secondary waste simulant based on the LAW melter off-gas SBS. Table 2.11 shows the target concentrations for the LAW and WTP-SW simulants (TTT 2009). Target concentrations of several of the minor constituents of interest were increased to make certain that FBSR off-gas and products will be detected in an effort to provide information for mass balance calculations and to measure the immobilization performance of the FBSR waste product and encapsulated product monolith. In the WTP-SW simulant, the concentration of Re (surrogate for ^{99}Tc) was increased by a factor of 10, the Ni and Pb by a factor of 100, the Ag by 1,000, and the Cs by 1,000,000. Target concentrations of Ba, Cd, Sb, Se, and Tl were increased to levels 1000× the analytical detection limit in the feed solution.

Table 2.10. Hanford LAW Simulant used in 2004 STAR Pilot-Scale Test (from Olson et al. 2004a)

Component	Target (g/L)	As Measured (g/L)
Al	1.7	1.8
Ca	-	0.025
Cr	0.54	0.50
Cs	0.00001	0.000014
K	0.48	1.9
Mg	-	0.0078
Na	120	130
Re	.096	0.050
Si	-	0.041
$CH_3CO_2^{-2}$	0.70	-
$C_2O_4^{-2}$	12	-
CO_3^{-2}	29	-
Total inorganic carbon	5.7	5.3
Total organic carbon	3.5	3.3
Cl^-	1.6	1.6
F^-	0.60	1.0
I^-	0.0017	0.0021
NO_2^-	20	20
NO_3^-	160	160
OH^-	13	-
PO_4^{-3}	4.7	4.5
SO_4^{-2}	8.6	8.3
Water	870	850
Specific Gravity	1.23	1.2

Table 2.11. Target Concentrations of LAW and WTP-SW Simulants (from TTT 2009)

Component	LAW Target Concentration (mole/L)	WTP SW Target Concentration (mole/L)	Makeup Reagent
Oxalate	0.0118	-	$Na_2(C_2O_4)$
Acetate	0.132	-	$Na(C_2H_3O_2)$
Hydroxide	0.74	1.564	NaOH
Carbonate	0.475	0.200	Na_2CO_3
Sulfate	0.09	0.005	Na_2SO_4
Chloride	0.0438	0.106	NaCl
Fluoride	0.0316	0.219	NaF
Iodide	0.013	0.001	NaI
Nitrite	0.424	0.036	$NaNO_2$
Phosphate	0.0492	0.007	$Na_3PO_4 \cdot 12H_2O$
Aluminum	0.0637	0.548	$Al(NO_3)_3 \cdot 9H_2O$, 60 wt% solution
Potassium	0.0124	0.010	KNO_3
Sodium	5.0161	2.668	$NaNO_3$
Nitrate	2.58487	1.991	[from other components]
Silver	0.00161	0.00086	$AgNO_3$
Arsenic	0.00137	0.00010	H_3AsO_4, 75 wt% solution
Barium	0.00751	0.00002	$Ba(NO_3)_2$
Cadmium	0.0042	0.00087	$Cd(NO_3)_2 \cdot 4H_2O$
Chromium	0.0104	0.00606	$Na_2Cr_2O_7 \cdot 2H_2O$
Cesium	0.013	0.01469	$CsNO_3$
Nickel	0.0106	0.00458	$Ni(NO_3)_2 \cdot 6H_2O$
Lead	0.00606	0.00131	$Pb(NO_3)_2$
Rhenium	0.0017	0.00113	$NaReO_4$
Antimony	0.00434	0.00160	Sb_2O_3
Selenium	0.00123	0.00247	SeO_2
Thallium	0.00202	0.00096	$TlNO_3$
Ammonium	-	0.292	NH_4NO_3
Boron	-	0.132	$Na_2B_4O_7 \cdot 10H_2O$
Silicon	-	0.018	$Na_2O \cdot SiO_2$, 37.6 wt% solution
Zinc	-	0.00729	$Zn(NO_3)_2.6H_2O$

The FBSR process has been in commercial use for a number of years at the Studsvik facility in Erwin, Tennessee, where LLW is processed (TTT 2003). At that facility, a wide variety of wastes are processed, including ion exchange resins, charcoal, graphite, sludge, oils, solvents, plastic filters, personal protective clothing, and cleaning solutions (TTT 2003).

Testing is currently underway at SRNL with a bench-scale steam reformer to confirm the results of the non-radioactive, pilot-scale test with Hanford LAW and LAW melter off-gas recycle simulant wastes (Jantzen et al. 2011). Secondary waste from the SRS Defense Waste Processing Facility HLW vitrification facility was shimmed to chemically resemble the Hanford off-gas recycle secondary waste.

A second campaign was conducted with SRS LAW shimmed to resemble Hanford LAW. Ninety-six grams of Hanford secondary-waste product and 600 grams of Hanford LAW product were prepared in the two campaigns. Characterization of the products is underway. The same mineral phases were identified in the radioactive testing as previously identified in the non-radioactive pilot-scale testing.

3.0 Waste Form Process Description

Classical steam reforming is a versatile process that decomposes organic materials through reaction with steam (Olson et al. 2004a). Steam reforming has been used on a large scale by the petrochemical industry to produce hydrogen for at least 65 years. If the material being reformed contains halogens, phosphorus, or sulfur, mineral acids are also formed (e.g., hydrochloric acid, phosphorous acid, phosphoric acid, and hydrogen sulfide) unless inorganic materials capable of scavenging these species are present in the waste or additives (Nimlos and Milne 1992; Olson et al. 2004a). Organic nitrogen is converted to N_2, and organic oxygen is converted to CO or CO_2 (Olson et al. 2004a). In the presence of a reducing agent such as organic carbon, nitrates and nitrites are converted to nitrogen gas (Vora et al. 2009).

The THOR® steam reforming process can destroy organic constituents of the initial waste fluids, including RCRA and *Toxic Substances Control Act* (TSCA) organics (Mason et al. 2003). In addition, the steam reforming process reacts with the organics to form carbon monoxide, hydrogen, and some hydrocarbon gases. With the addition of oxygen, these gases oxidize to form carbon dioxide and water vapor.

The THOR® FBSR process is being used commercially to process both liquid and solid low-level radioactive waste streams, including ion-exchange resins, charcoal, graphite, sludge, oil, and solvents that emit up to 400 R/hr radioactivity (Mason et al. 2003).

In the application of FBSR to Hanford wastes, a clay mineralizing agent is added to the wastes in the feed tank. The resulting slurry is injected into the fluidized bed. The bed is fluidized with superheated steam at 600º to 800 ºC and near-ambient pressure. A carbon source, such as coal, wood product, or sucrose, is injected into the bed as a fuel source and reducing agent. Within the fluidized bed, the waste-feed droplets coat the bed particles and rapidly dry. Nitrates, nitrites, and organics are destroyed (TTT 2009; Vora et al. 2009).

In the steam environment at 700º to 750 ºC, the clay mineralizing agent injected with the wastes becomes unstable as hydroxyl groups are driven out of the clay structure (Jantzen 2008). The clays become amorphous, and the silicon and aluminum atoms become very reactive. Alkali elements, including sodium, potassium, and cesium in the wastes, “alkali activate” the unstable Al^{3+} to form the new mineral phases. The other waste component cations and anions are captured in the cage structures and the sodium aluminosilicate minerals form.

The granular product is removed from the FBSR either as product from the bottom of the bed or as particulates removed from the fluidizing gases by the HTF. These two materials are then combined and encapsulated in a binder for final disposal.

3.1 Waste Form Ingredients

Kaolin clay, the aqueous waste stream, steam, and a carbon source are the only ingredients for the FBSR sodium aluminosilicate granular product.

3.1.1 Kaolin Clay

Several sources of kaolin clay have been used in the FBSR pilot-scale testing program. Table 3.1 lists some of the properties of those that have been used (Olson et al. 2004a, b). Table 3.2 lists the chemical composition of the kaolin clays that were used in the 2008 Hanford LAW and WTP-SW tests at the Hazen Research facility.

The kaolin clay type was selected with the appropriate Al:Si mole ratio that would suitably react with the Na and anions in the waste liquids. Usually, a ternary phase diagram (such as the one depicted in Figure 3.1) shows the target region of compositions that is thought to be the most favorable for producing the desired mineral products (Crawford and Jantzen 2007). See Olson et al. (2004a) and TTT (2009) for similar ternary diagrams for Hanford LAW and WTP-SW wastes. The most favorable atomic ratios that would produce the desired nepheline and sodalite products are thought to be M/Si = 1−1.33, M/Al = 1−1.33, Al/Si ≥ 1, and M/(Al+Si) = 0.5–0.67, where M represents an alkali metal, mostly Na in this case; the atomic ratios provide guidelines because there may be significant substitution of different alkali and alkaline earths, and some Fe for Al, in these feldspathoid minerals (Olson et al. 2004a). SRNL has developed a spreadsheet called MINCALC^{TM} that can be used as a tool to select the clay formulation and carbon addition and to make adjustments, such as accounting for extra aluminum and potassium in the wastes (Crawford and Jantzen 2007; Pareizs et al. 2005).

Four types of kaolin clay were investigated for use as a mineralizing additive in the INEEL pilot-scale experiment. Each clay was evaluated based on XRD analyses, particle-size analyses, whole element chemistry, and rheological properties (Olson et al. 2004b). The mineralizing agent needs to have a Si:Al ratio that will react with the liquid waste and produce desired minerals.

Additional considerations for choosing the optimum mineralizing additive include the particle-size distribution, which is optimized to make sure that as much clay as possible reacts with the liquid waste as well as eliminating clays that contain additional elements that will not react to form the desired mineral phases. SNOBRITE® clay was chosen for the INEEL pilot-scale study because of its favorable properties, but this material was not available; OptiKasT® clay was then chosen instead because of its similar properties (Olson et al. 2004a,b).

3.1.2 Carbon

Different reductants (e.g., charcoal or carbon) are used in the FBSR process to aid in reducing metals and removing nitrate. For example, different types of carbon were considered for use as reductants in the INEEL pilot-scale experiment. Carbon was evaluated based on reactivity, particle size, attrition resistance, moisture content, loss on ignition, and the ash composition. A wood-based carbon was chosen based on its efficient performance (Olson et al. 2004a,b) (see Table 3.3). Appendix C of the Olson et al. report (Olson et al. 2004a) provides a good description of a selection of carbon reductants. Key parameters were the particle size and the quantity of usable carbon as determined through thermogravimetric analysis.

Coal was used in the 2008 Hazen Research facility FBSR testing with Hanford LAW and WTP-SW simulated wastes (TTT 2009).

3.1.3 Starting Bed Material

The material that will be chosen for the fluidized bed reactor starting material must be dense and inert and have a high heat capacity because the process is typically conducted at approximately 725 °C (Olson et al. 2004b). Additional bed materials that meet these criteria and were considered for a pilot-scale steam reformer developed by INEEL include dolomite, sintered bauxite beads, nepheline syenite, and sintered calcium silicate (Olson et al. 2004b). The material chosen for the bed material was chosen based on composition, melting point, resistance and durability, particle size, and availability of the material. The bed material that was chosen for this pilot-scale study conducted at INEEL was 70-grit alumina. The alumina was chosen because of its attrition resistance and inertness (Olson et al. 2004a). Alumina was also used as the starting bed material for the 2008 Hanford LAW and WTP-SW pilot-scale tests at the Hazen Research facility.

3.2 Process Steps

After startup, the FBSR process is straightforward. The clay mineralizing agent is blended with the aqueous wastes in the feed tank. The resulting slurry is fed into the FBSR, and the granular product is removed through the bottom of the FBSR and through the filters for the fluidizing gases leaving the bed. The granular product is collected and allowed to cool before sending to the binder station for encapsulation into a monolith.

3.3 Process Times and Temperatures

Typically, glass and ceramic types of waste forms are created at temperatures ranging from 1000 to 1500 °C, whereas FBSR waste forms are made at temperatures ranging from 540 to 800 °C (Jantzen 2008; Vora et al. 2009; Williams et al. 2010).

3.4 FBSR Granular Product Encapsulation

The FBSR granular product will be encapsulated to meet disposal system requirements for compressive strength and to minimize the dispersability of the material. Several binders have been tested (Jantzen 2006b; TTT 2009), but further testing and development is anticipated before a final form is selected. Simple, inexpensive binders, such as a cementitious material, a geopolymer, or Ceramicrete, are likely candidates.

Table 3.1. Properties of Kaolin Clays Used in FBSR Pilot Scale Tests (from Olson et al. 2004a, b)

Clay	SNOBRITE	OptiKasT	Troy	K-T Sagger XX
Major Phases	Kaolinite (PDF# 75-1593) $(Al_2O_3 \cdot 2SiO_2 \cdot 2H_2O)$	Kaolinite (PDF# 75-1593) $(Al_2O_3 \cdot 2SiO_2 \cdot 2H_2O)$	Kaolinite (PDF# 75-1593) $(Al_2O_3 \cdot 2SiO_2 \cdot 2H_2O)$	Kaolinite (PDF# 78-1996) $(Al_2O_3 \cdot 2SiO_2 \cdot 2H_2O)$
Minor phases	Muscovite (PDF# 07-0042) $(K, Na)(Al, Mg, Fe)_2$-$(Si_{3.1}Al_{0.9})O_{10}(OH)_2$ Rutile (TiO_2) possible	Muscovite (PDF# 07-0042) $(K, Na)(Al, Mg, Fe)_2$-$(Si_{3.1}Al_{0.9})O_{10}(OH)_2$	Muscovite (PDF# 86-1385) $((K_{0.86}Al_{1.94})(Al_{0.965}Si_{2.895}O_{10})$-$((OH)_{1.744}F_{0.256})$ Quartz (SiO_2) possible	Muscovite (PDF# 07-0042) $(K, Na)(Al, Mg, Fe)_2$-$(Si_{3.1}Al_{0.9})O_{10}(OH)_2$ Quartz (SiO_2) Rutile (TiO_2)
Si:Al atom ratio	1.02	1.04	1:1.21	1:1.69
Total moisture (wt %	14.20%	15.15%	14.65%	10.6%
Particle size (wt% less than) 10% –	0.82 µm –	0.74 µm –	1.83 µm –	1.34 µm –
50% –	5.00 µm –	4.22 µm –	14.83 µm –	6.55 µm –
90%	20.8 µm	15.9 µm	57.1 µm	21.5 µm
Particle density	2.77 gm/cc	2.69 gm/cc	2.74 gm/cc	2.73 gm/cc

PDF# = powder diffraction file number

Table 3.2. Composition of Mineralizing Clay Used for WTP SW Simulant (from TTT 2009)(a)

	Clay Type		
Oxide	OptiKasT %	Sagger XX %	55% OptiKasT / 45% Sagger XX Mixture %
Al_2O_3	37.76	31.48	34.94
SiO_2	44.67	55.09	49.35
Fe_2O_3	0.55	0.84	0.68
TiO_2	1.67	0.63	1.20
CaO	0.04	0.13	0.08
MgO	0.03	0.15	0.08
Na_2O	0.02	0.09	0.06
K_2O	0.11	0.65	0.36
P_2O_5	0.07	0.00	0.04
H_2O	15.08	10.94	13.22
Sum	100.0	100.0	100.0

(a) Table 4-3, “Report for Treating Hanford LAW and WTP SW Simulants: Pilot Plant Mineralizing Flowsheet,” April 2009, THOR Treatment Technologies, LLC.

Table 3.3. Characteristics of Carbon Reduction for SAIC STAR FBSR Tests (from Olson et al. 2004a)

Supplier	Berger Brothers, Chicago, IL
Type/Size	Wood base, −0.371 inch, +0.185 inch
Moisture (% of sample)	3.13
Ash at 650 °C (% of dried sample)	5.38
Ash at 750 °C (% of dried sample)	5.14
Loss on Ignition (% loss of undried sample)	95.0

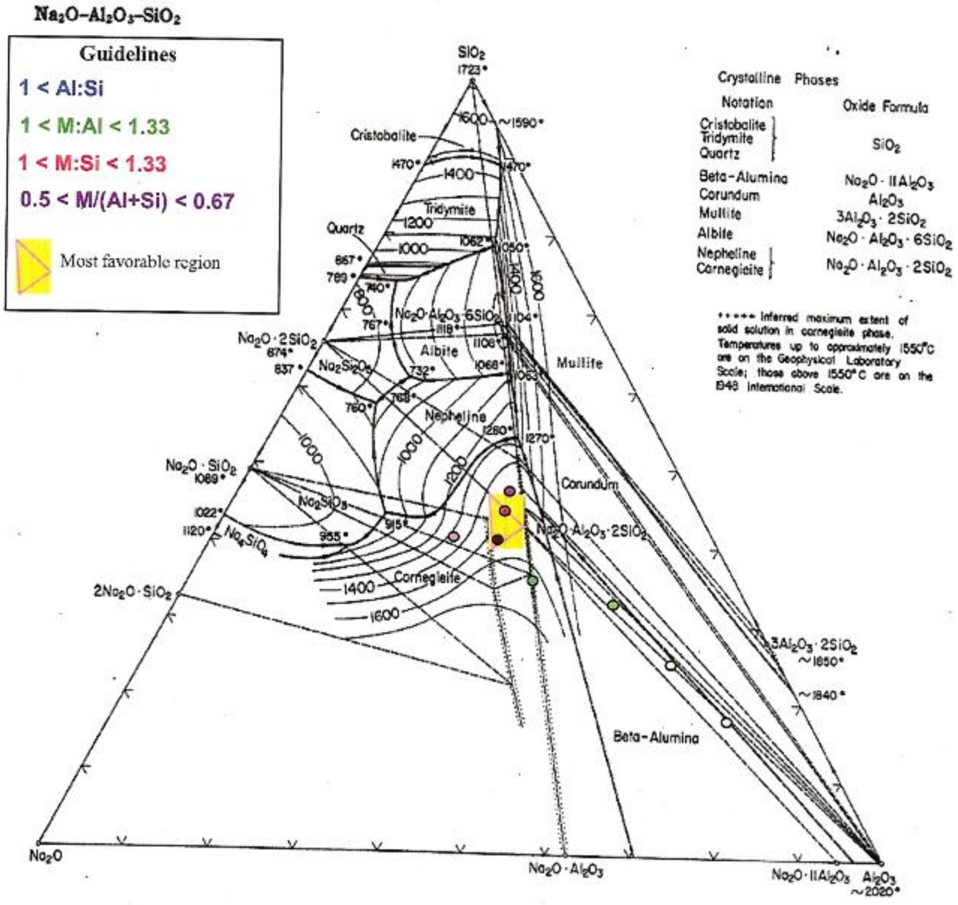

FIG. 501.—System $Na_2O-Al_2O_3-SiO_2$; composite.

E. F. Osborn and Arnulf Muan, revised and redrawn "Phase Equilibrium Diagrams of Oxide Systems," Plate 4, published by the American Ceramic Society and the Edward Orton, Jr., Ceramic Foundation, 1960.

DMR Samples		g clay / L	HTF Samples		g clay / L
○	4504	228	●	4508	228
○	4531	276	●	4546	276
●	4637	339	●	4649	339
●	4726	200	●	4728	200

Figure 3.1. Ternary Diagram Showing Guidelines for Kaolin Clay Selection (from Crawford and Jantzen 2007)

4.0 Waste Form Production Description

The FBSR process was designed by TTT to treat radioactive wastes (U.S. Patents 6,280,694; 7,001,800; 7,125,531). The steam reforming process thermally treats wastes at temperatures ranging from 625 to 800 ºC using a fluidized bed reformer (Vora et al. 2009). During mineralization with superheated steam, organic matter is converted to carbon dioxide, and nitrates and nitrites are reduced to nitrogen. The non-volatile solids in the residue are converted to stable crystalline minerals, dependent on what mineralizing material is added with the waste feed, such as aluminosilicates that incorporate contaminants.

The FBSR process has been demonstrated at a pilot scale with Hanford LAW and WTP-SW non-radioactive simulants, and a bench-scale demonstration with a radioactive Hanford simulant is planned as part of the ART program funded by DOE and other DOE Environmental Management (EM) funding (TTT 2009; Vora et al. 2009). DOE selected FBSR as the technology to treat approximately 1,000,000 gallons of SBW at the INL to form a carbonate material for disposal at the U. S. Department of Energy Waste Isolation Pilot Plant (WIPP). The Integrated Waste Treatment Unit at Idaho is currently under construction. The FBSR technology was also selected by DOE in 2009 to treat Tank 48H wastes at SRS to remove organics from the wastes and return the resulting carbonate material to the tank farm or to the vitrification facility. The design is underway for that FBSR facility.

The steam reforming treatment of liquid LAW and WTP-SW converts the liquid waste to a mineralized product that is water insoluble. Through the process, the water contained in the waste is evaporated, the nitrates and nitrites are converted to nitrogen gases, and sodium is converted into sodium aluminosilicate solid phases. Pilot-scale FBSR systems that have been used to demonstrate processing of Hanford wastes include the SAIC STAR facility in Idaho and the Hazen ESTD facility located in Golden, Colorado.

The FBSR system is composed of the following components (Olson et al. 2004b):

1. a feed for gases, liquids, slurries, and small solids
2. the fluidized bed reactor vessel
3. the solid and product collection
4. the off-gas treatment
5. the monitoring and control of the system.

There is no information available in the literature on a flowsheet for encapsulating the FBSR granular product in a binder to produce a monolithic waste form.

4.1 Fluidized Bed Steam Reformer Process Description

For mineralizing nitrate waste, the FBSR process uses a single reformer, the denitration and mineralization reformer (DMR), as shown in Figure 4.1. The operating temperature in the DMR is maintained at 700 to 750ºC for generating the aluminosilicate end product. The flow diagram shows the feed preparation, denitration and mineralizing, and off-gas portions of the FBSR process. All mineralization reactions take place in the DMR. Granular products are removed from the bottom of the DMR, and finer product solids are separated from the process outlet gases by the product separation filter (PSF). The finer PSF mineral solids and the granular mineral solids from the DMR are combined in the

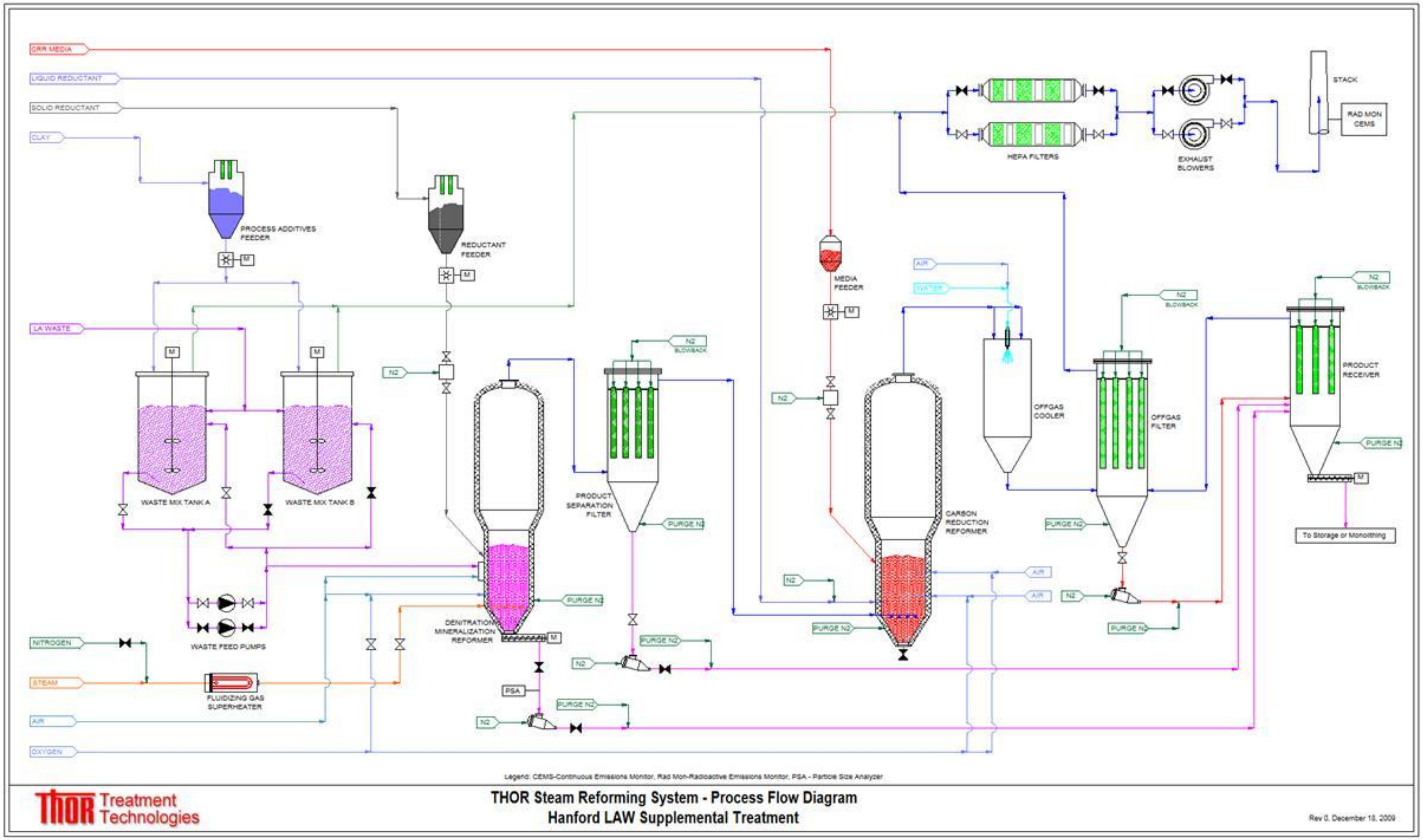

Figure 4.1. Dual-Stage FBSR Process Flowsheet (TTT 2009)

monolith preparation system (not shown).

The process outlet gases are treated in the off-gas treatment system to meet air permit emission limits. As there are several proven methods to produce final monolithic product waste forms, the monolith preparation system is shown as a process unit operation block. The following section provides a brief description of the principal mineralizing components of the FBSR flowsheet. Additional details are available at the TTT website (www.thortt.com) (Jantzen 2002; Olson et al. 2004a, Soelberg et al. 2004).

4.1.1 Denitration and Mineralization Reformer

The DMR is a fluidized bed reformer with the bed media being fluidized with superheated steam injected through a distributor at the bottom of the refractory-lined vessel. A small amount of oxygen is added to the fluidizing steam added to the bed to promote the oxidation of carbon to provide energy generation in the bed. Compressed air is used to atomize the waste/clay slurry into the bed. Granular carbon is also fed directly into the bed to provide energy for the process and to generate small amounts of reductive gases, namely carbon monoxide and hydrogen, via the water gas reaction. The DMR bed material consists of accumulated mineral product granules that are fluidized by the low-pressure steam. The mineral products are formed by the hydrothermal reaction of the alkali metals, mainly sodium and potassium, and inorganics in the waste with the added clay (aluminosilicate) as the waste/clay slurry is injected into the bed by the waste feed injectors. The waste/clay slurry is atomized upon entry into the bed by a metered flow of atomizing air where the small droplets of waste/clay slurry are converted into stable, leach-resistant, mineral compounds (Figure 4.1).

The waste feed is introduced into the fluidized bed as fine spray. The waste feed dries the moment it contacts the heated fluidized bed, and the nitrates and nitrites in the dried feed react with the reductive gases to produce mainly nitrogen gas with traces of NO_x. The non-volatile contaminant constituents, such as metals and radionuclides, are mineralized by being incorporated into the final bed product. The end products are continuously drawn off the bottom of the DMR and transferred by an auger into a PR.

4.1.2 Off-Gas Treatment System

The off-gas treatment system provides high-efficiency filtration and oxidation of any residual volatile organics and small amounts of carbon monoxide and hydrogen from the DMR. The process off-gas from the DMR is routed into a PSF to trap small particles of mineral product. It then passes through the carbon reduction reformer (CRR) to reduce residual NO_x to N_2 in the lower reducing zone and to oxidize CO, H_2, and the residual hydrocarbons into CO_2 and water in the upper oxidizing stage of the CRR. No additional NO_x abatement or acid gas removal is required because the nitrates and nitrites are converted into nitrogen gas inside the DMR and CRR with a very high efficiency (TTT 2009). Additionally, the acid gases (mainly S, Cl, and F) are converted directly into stable, water-insoluble compounds such that no wet scrubber is required to remove acid gases in the off-gas treatment system. The off-gas from the CRR then passes through a high-efficiency particulate air (HEPA) filter to remove any particulates and then is cooled in an off-gas cooler and passed through another set of HEPA filters and a mercury adsorber (if needed) before being exhausted out of a stack. The FBSR process outlet gases are compliant with Maximum Achievable Control Technology (MACT) limits for metals, HCl/Cl_2, particulates, dioxins/furans, volatile and semi-volatile organic compounds, total hydrocarbon, and carbon monoxide as well as site discharge limits for NO_x and SO_x (Vora et al. 2009; TTT 2009).

4.2 Other Flow Sheets

A simplified flow schematic of the steam reforming process is shown in Figure 4.2 and Figure 4.3. These schematics are for the SAIC STAR test facility used in the early FBSR testing.

The THOR® system and its components include the feed system, the Fluidizing Gas (FG) Flow System, the DMR, the PR, the HTF, the CRR, and the off-gas treatment (TTT 2009).

4.3 Fluidized Bed Steam Reformer Test Facilities

Several TTT-designed FBSR testing platforms have been built and used to demonstrate steam-reforming technology for immobilizing radioactive waste. Bench- and pilot-scale facilities have been assembled to demonstrate the treatment of both simulated and radioactive waste streams.

The following sections describe existing FBSR test platforms for Hanford LAW waste immobilization. The capabilities reviewed are:

- Pilot Scale—Hazen Engineering Scale Technology Demonstration (ESTD) facility located in Golden, Colorado
- Bench Scale—Bench-scale steam reformer (BSR) non-radioactive system at SRNL
- Bench Scale—BSR radioactive system at SRNL
- Bench-scale—Studsvik bench-scale steam reformer (BSSR) at the Teledyne Brown Engineering Laboratory in Knoxville, Tennessee.

4.3.1 Hazen Engineering Scale Technology Demonstration Facility

The Hazen ESTD facility, located in Golden, Colorado, has been used for non-radioactive simulant immobilization demonstrations of several potential radioactive waste streams including the 2008 demonstrations with Hanford LAW and WTP-SW (TTT 2009). The facility has access to 6-in., 15-in., and 22-in. FBSRs, all of which have been used in qualification testing of the THOR® process. This test platform has successfully reformed the simulated radioactive waste into water-soluble carbonate or insoluble mineralized matrices, depending on the process additives used.

This process can be represented by the flow diagram for the INL SBW mineralized test program conducted in November and December of 2006, which is shown in Figure 4.4. This process flow diagram identifies each of the major THOR® system components used in this demonstration. The major components include liquid waste preparation and feed tanks, the fluidizing gas supply system, the DMR, product receivers, the HTF, the CRR, and the off-gas treatment system.

This test platform was successfully used to run scoping and production tests resulting in the conversion of 3014 gallons of SBW simulant to 14,101 pounds of granular solid product during 348.6 hours of “feed-on” operation.[1] The following abbreviated process description of the THOR® ESTD INL SBW mineralized test program is presented as a viable Hanford LAW simulated-waste testing capability.

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[1] Pilot Plant Report for Treating SBW Simulants: Mineralizing Flowsheet, RT-002, THOR Treatment Technologies, LLC, July 2007.

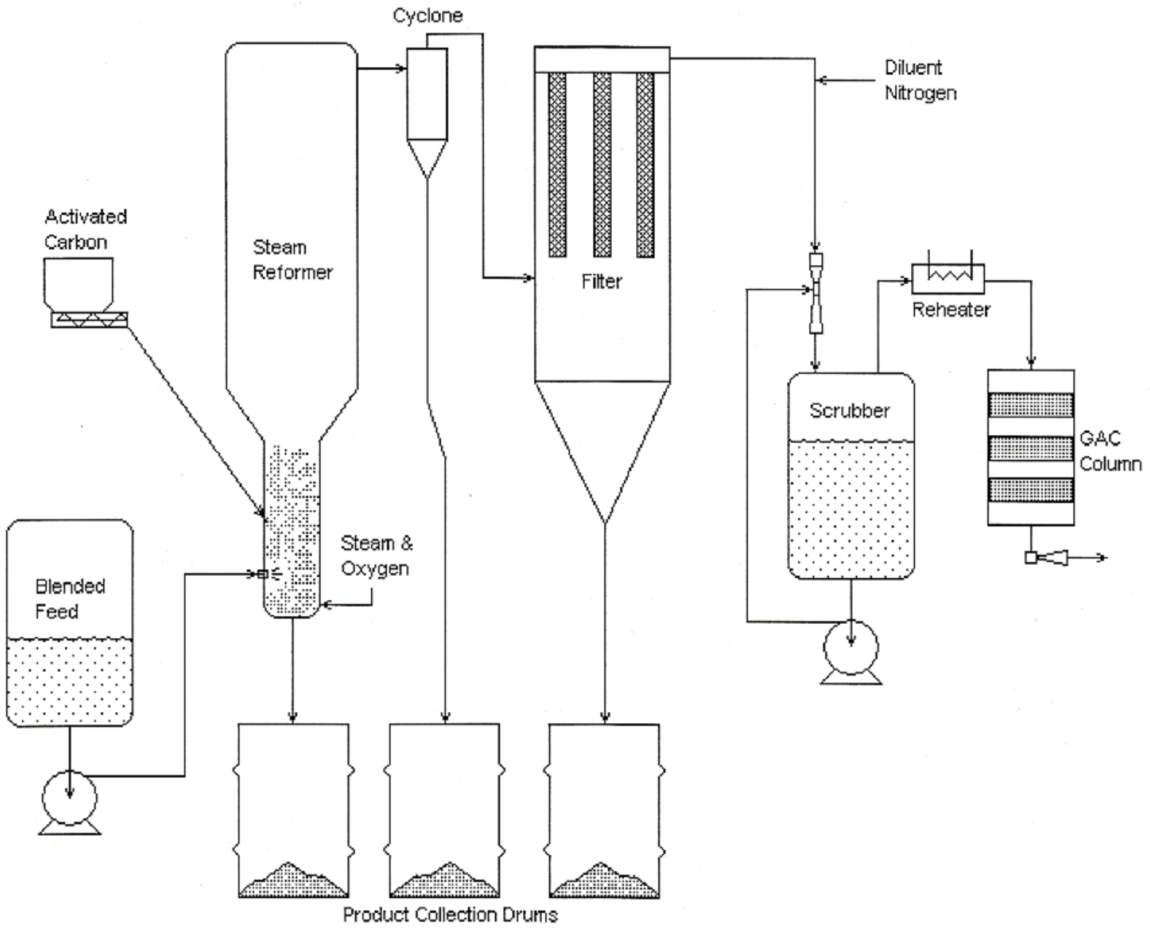

Figure 4.2. Steam Reforming Process Flow Diagram (Marshall et al. 2003)

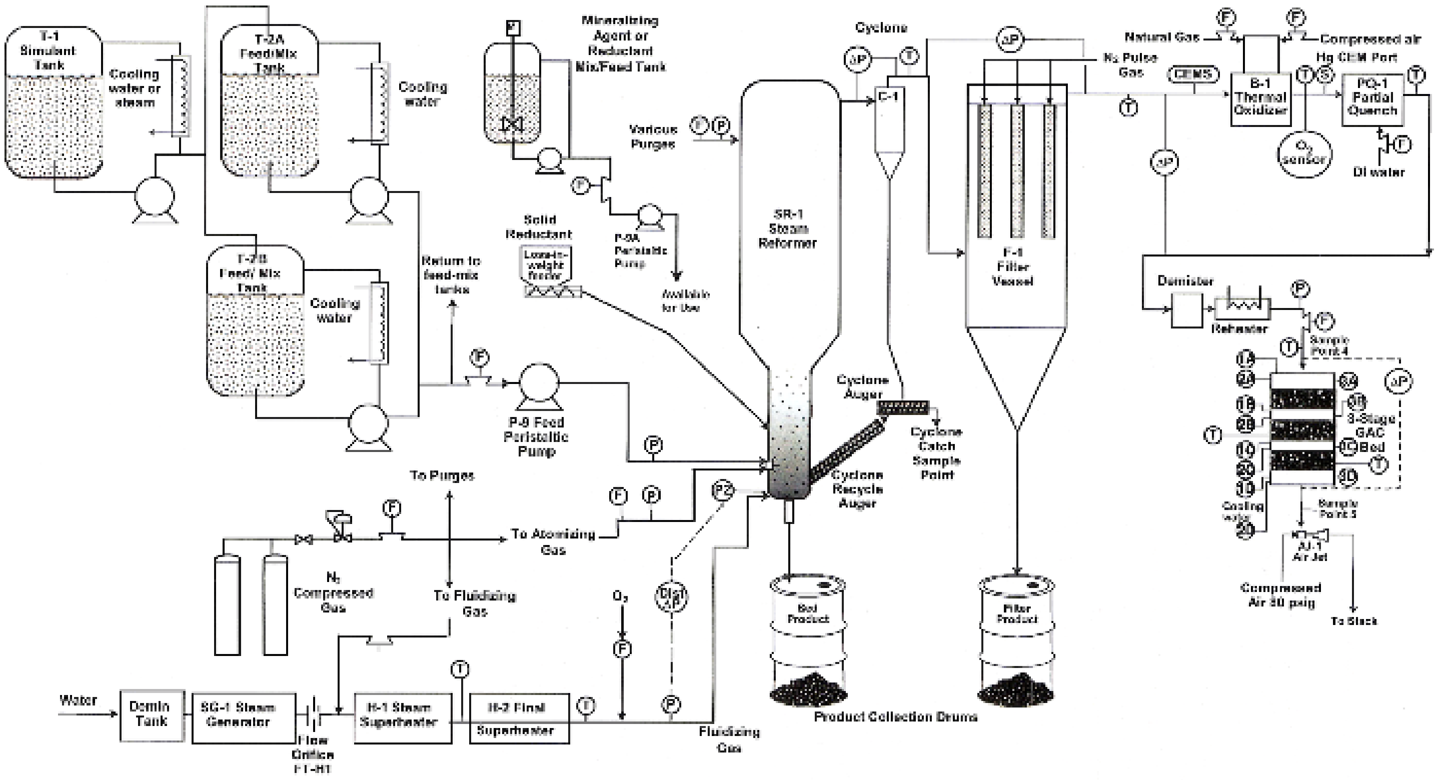

Figure 4.3. Process Flow Diagram for the Fluidized Bed Mineralizing Steam Reforming Demonstration (Olson et al. 2004b)

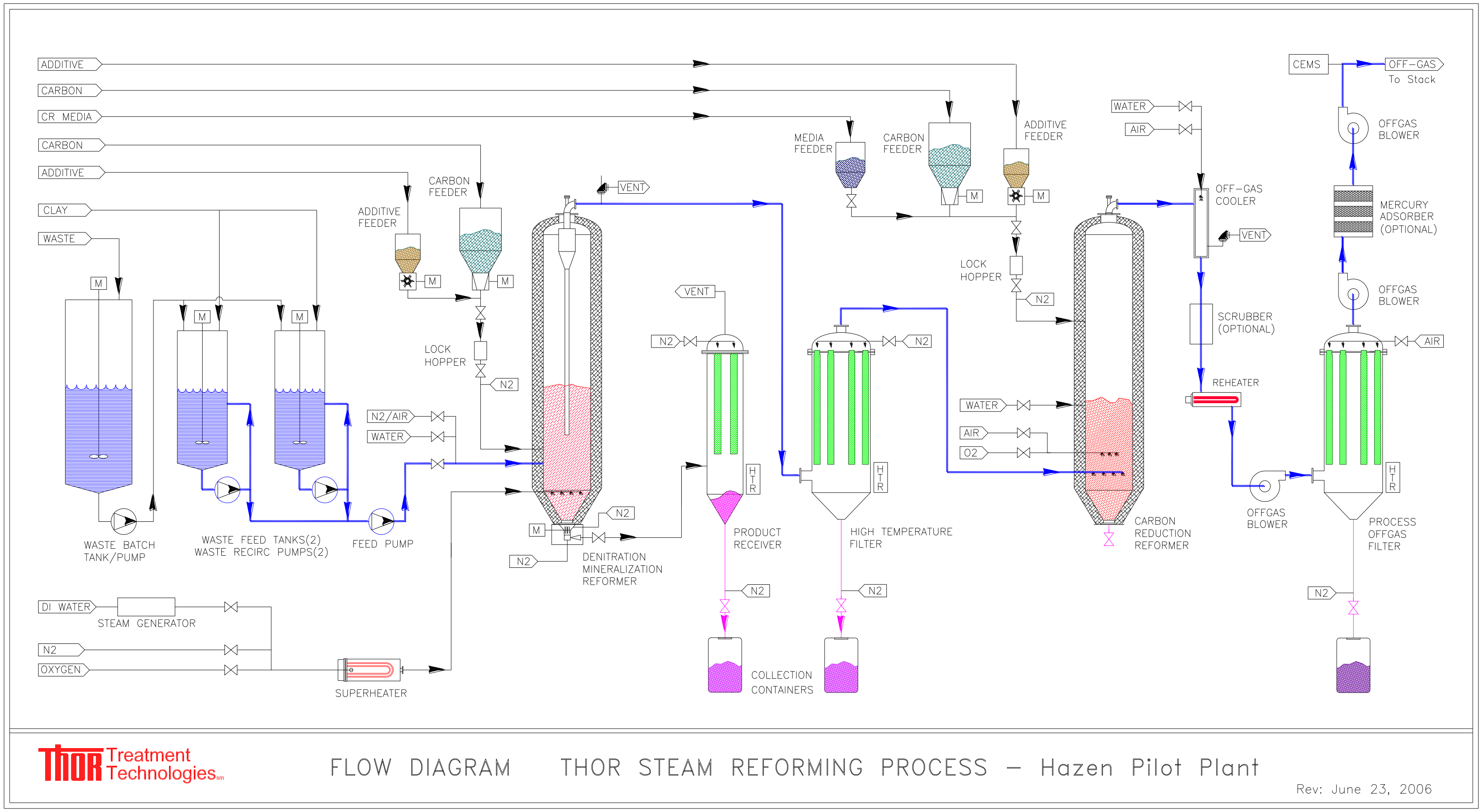

Figure 4.4. Hazen Engineering-Scale Flow Diagram (TTT and WGI 2007)

4.3.2 Hazen FBSR Subsystem Descriptions

4.3.2.1 Liquid Simulant Preparation and Feed

The liquid simulant preparation and feed system included a 1,600-gal. stainless steel surrogate tank, waste feed makeup tanks with mixers, transfer pumps, waste feed day tanks with mixers, a tank and pump for organic hazardous constituents, a flow-control pinch valve, a feed filter, and surrogate feed waste injectors.

The feed arrangement consisted of a surrogate-waste mixing tank and two waste feed day tanks. Each tank was outfitted with a mixer to keep target constituents suspended and to provide agitation to dissolve solid reagents. The surrogate-waste mixing tank was used for batch preparation of waste feed liquids before adding undissolved solids, heavy metals, and mineralizing additives. This surrogate liquid feed stream was transferred to two waste feed day tanks to which the undissolved solids, heavy metals, and mineralizing additives were added and suspended. Recirculation pumps aided in keeping components suspended. A slipstream drawn off the day tank recirculation line was used to feed the DMR.

An auxiliary tank with a liquid metering pump was used to meter the principal organic hazardous constituents, at a flow rate of approximately 0.33 kg per hour, into the process feed line.

4.3.2.2 Fluidizing Gas System

The fluidizing gas system consisted of a steam generator, nitrogen and oxygen gas feed, steam superheaters, flowmeters, control sensors, and injection nozzles. Steam or a mixture of steam and oxygen was used to fluidize the DMR during normal operations. Oxygen reacts with the carbon and hydrogen to generate process heat, carbon dioxide, and water vapor. The concentration of oxygen injected is therefore controlled for the appropriate process conditions: startup, normal operation, or reaction adjustment. The temperature of the DMR was controlled by adjusting the oxygen input to the DMR.

A steam generator was used to provide steam for the fluidizing gas system. This generator was capable of providing up to 500 pounds per hour of low-pressure steam, but for this demonstration was used to supply 70 to 200 pounds per hour. The steam or steam-oxygen mixture was flowed through two electric super heaters, in series, to increase the temperature to 600 °C before introduction into the DMR.

The fluidizing gas super heaters were used to preheat nitrogen as the fluidizing gas during DMR startup preheating operations. These heaters were the major heat load for the initial heat up of their reformer because external fluidized bed vessel heaters were not provided. During initial startup and preheating of the DMR, these fluidizing gas super heaters were capable of heating the fluidizing nitrogen to about 700 °C.

The total gas flow rate was controlled to maintain the DMR temperature and pressure profiles and to fluidize the FBSR bed solids. The total gas flow was divided by the bed cross-sectional area to give the superficial space velocity (SSV) in the bed. The minimum required fluidizing velocity was determined with the Wen and Yu correlation,[1] and the SSV was selected to exceed the minimum fluidizing velocity for the average bed particle size.

The oxygen introduced into the bed generated heat within the DMR by reacting with added carbon reductant and with the carbon monoxide and hydrogen produced in the bed by the steam reforming reactions. The additional oxygen was added through the steam fluidizing distributors to maintain the desired bed temperature range, typically 700 °C to 750 °C, for insoluble mineralized product formation.

4.3.2.3 Denitration and Mineralization Reformer

The 15-in. inside-diameter, fluidized steam reformer vessel, which was made of carbon steel and was refractory-lined, was used for the SBW waste demonstration. This reactor was fabricated to provide ports for simulant feed, fluidizing nozzles, particulate carbon reductant feed, a solids removal auger, and a process gas outlet. Figure 4.5 is a photograph of the DMR (to the left). The pilot facility has successfully demonstrated conversion of simulated waste plus mineralizing additive at DMR feed rates of about 0.2 gallons per minute.[2]

The DMR vessel was modified for continuously metered solids addition of particulate carbon reductant and recycled bed materials (mainly carbon recycle). Solids were added via two independent solids feeders. The solids were discharged into a small airlock chamber bounded by two valves on either side that were operated sequentially to form a lock hopper. This injection chamber was purged with nitrogen to exhaust atmospheric air and provide some motive force to inject the carbon solids into the DMR. Automatically controlled screw augers with load cells were used to monitor and control the feed rates of the carbon reductant and other solids into the lock hoppers.

A pneumatically controlled pinch valve was used to control the feed rate of the liquid feed into the DMR through one of two atomizing feed nozzles, only one of which was operated at a time. The feed nozzle not in use was purged to prevent bed solids from entering the nozzle orifice. The flow rate of the atomizing gas was automatically controlled with an integrated mass flowmeter. Typically, air was used, but pure nitrogen and/or a mixture of air and nitrogen could have been used.

The DMR bed was operated to maintain a fluidized bed depth of about 36 to 42 inches. The accumulated solids product in the DMR bed was removed via a removal auger and nitrogen jet located at the bottom of the bed. The nitrogen jet below the auger transferred the hot bed solids to a receiver vessel. Sample lines and valves located on the side of the vessel facilitated periodic DMR bed material sampling.

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[1] D Kunii and O Levenspiel. 1991. *Fluidization Engineering,* 2nd Edition, Butterworth-Heinemann, Newton, Massachusetts.

[2] Table 8-1, DMR Input Flow Rates Used in the DMR Process Gas Calculations for the Off-gas Sampling Periods, *Report for Treating Hanford LAW and WTP SW Simulants: Pilot Plant Mineralizing Flowsheet, 002 Rev. 1,* THOR® Treatment Technologies LLC, April 2009.

Figure 4.5. Denitration and Mineralization Reformer (left) and High-Temperature Filter (right)(TTT and WGI 2007)

The DMR was designed with an external cyclone. The intent of the cyclone was to return a majority of the particulate matter greater than 100 microns in size back to the fluidized bed through an internal return line that extended into the bed. This reformer was also designed with an enlarged disengagement section (freeboard) to reduce the gas velocity and reduce the amount of particulate matter carried to the top of the reformer. Subsequent updates to the DMR have resulted in removing the cyclone in favor of an extended disengaging section at the top of the unit to passively separate many of the solid fines and return them to the bed. This configuration was used for the ART Project tests.

4.3.2.4 Product Receiver

When the accumulated granular product solids in the fluidized bed in the DMR exceeded the 42-in. bed height upper limit, operators would manually transfer a quantity of bed product to the product receiver. The bed product was pneumatically transferred from the DMR and collected in a vertical, cylindrical filter vessel with a conical bottom. This filter vessel was fitted with four sintered metal, candlestick-type filters. The filters could be manually cleaned by remotely actuating a nitrogen gas pulse.

The off-gas outlet from the product receiver was returned to the freeboard of the DMR such that the gas removed from the bottom solids auger was reintroduced into the DMR. The product collection vessel provided a residence time for the product to cool before collection and storage in 55-gal. drums. Grab samples could be collected from the cooled collection vessel before being placed in the storage drums.

The Hazen test facility was designed with the option to recycle some of the granular product back into the DMR to maintain the required particle-size distribution in the bed. In addition, large carbon pieces removed with the bed products can be separated from the bed products and recycled to the DMR for reuse. The product would have to be screened offline and if required, returned on a semi-continuous basis to the DMR bed through the solids additive auger feeder and airlock system. Subsequent testing and processing has indicated that the bed bottoms and solids collected by the HTF can be encapsulated without the need for recycling the product fines.

4.3.2.5 High-Temperature Filter

The HTF is shown on the right in Figure 4.5 and was a filter vessel used to receive the process gases and elutriated fines off the top of the DMR. The filter housing was to remove and collect the fines before feeding the DMR process gases to the CRR. The HTF vessel was a vertical, cylindrical filter vessel modified with 18 sintered metal or silicon carbide candlestick type filters. The filters were connected to an automated, nitrogen-gas, back-pulse manifold that allowed for the cleaning of the filters while online. The pressure drop across the filters was measured with pressure sensor ports in the vessel and in the gas outlet line downstream of the vessel. This filter media differential pressure was used to initiate the automated filter or pulse-back function. External electrical heaters were used to maintain the filter elements and vessel at above 400 °C during normal operation.

Product solids were drained and collected with systems similar to the DMR product receiver. The HTF vessel provided a residence time for the fine mineral product to cool to about 200 °C before removal and storage in 55-gal. carbon steel drums. Grab samples could be collected from the cooled collection vessel before being placed in the storage drums.

4.3.2.6 Carbon Reduction Reformer

The CRR was a cylindrical, 24-in. inside-diameter vessel. It was made of carbon steel, was refractory-lined, had a fluidized bed, and was operated in series with the DMR. A refractory sleeve near the bottom of the reactor reduced the lower bed diameter to 17 inches.

The hot process gas from the DMR, filtered through the HTF, consisted primarily of water vapor, nitrogen, carbon dioxide, small amounts of carbon monoxide, hydrogen, methane, and other short-chain organics as well as traces of acidic gases. This gas was introduced at the bottom of the CRR to fluidize the bed media. A mixture of oxygen and nitrogen gases was injected through two sets of nozzles above the CRR fluidizing gas distributor. Under normal operating conditions, the zone below the oxygen injectors operated under strongly reducing conditions to facilitate additional NO_x conversion. In the zone above the oxygen/nitrogen gas injection nozzles, the CRR bed operated in an oxidizing mode to convert residual carbon monoxide, hydrogen, and organics from the DMR to carbon dioxide and water vapor. The CRR vessel had several insertion and injection ports; however, only the middle and upper gas nozzles were used during the mineralizing test. Figure 4.6 through Figure 4.8 show the top, middle, and bottom views of the CRR.

Figure 4.6. Carbon Reduction Reformer: Top (TTT and WGI 2007)

Figure 4.7. CRR: Middle (TTT and WGI 2007)

Figure 4.8. CRR: Bottom (TTT and WGI 2007)

The CRR was fabricated to provide for initial and periodic batch additions of alumina bed media and supplemental carbon reductant. Bed media were added to replace media lost to attrition and elutriated media loss, and supplemental carbon was added as it was continuously converted to carbon dioxide. The carbon reductant was added to the CRR through a loss-in-weight screw auger feeder and the alumina bed media by manual batch addition. The carbon reductant feeder introduced material into the reformer much like the DMR feeder. The solids auger discharged solids into a small airlock chamber bound by two valves that operated sequentially to form a lock hopper. Nitrogen gas was used to purge the atmospheric air from the lock hopper and provided motive force to inject the carbon reductant into the CRR. The CRR bed level was operated at a height of 26 to 36 inches.

The oxygen flow rate into the in-bed oxygen distributor was automatically controlled to maintain the CRR bed temperature within ±15 °C of the test temperature set point and to maintain a set outlet oxygen concentration in the CRR off-gas at about 2% to 10% by volume. The nominal gas residence time in the CRR was 2.5 to 3.0 seconds.

4.3.2.7 Off-Gas Treatment System

The off-gas treatment system consisted of an off-gas cooler, off-gas reheater, process off-gas filter, mercury absorber, and off-gas blowers. The off-gas cooler consisted of a direct contact, deionized water sprayer inserted into a 24-in.-diameter vessel downstream of the CRR. The cooler was designed to reduce the temperature of the CRR off-gas to as low as 130 °C in a fraction of a second.

The off-gas exiting the cooler was saturated with water vapor, and to prevent moisture from condensing and damaging off-gas equipment, the entire off-gas system was insulated to maintain the off-gas system above 120 °C. An electric reheater was used to reheat the gas above the dew point. The reheater raised the off-gas temperature from ~95 °C to an operating range of 130 °C to 190 °C. This off-gas reheater was removed for the LAW and WTP-SW tests.

An off-gas blower provided motive force from the off-gas cooler and reheater to the process off-gas filter. The process off-gas filter was installed downstream of the off-gas reheater and was used to remove and collect any fine solids elutriated from the CRR. It was a vertical vessel designed for high-temperature-rated, bag-type or candlestick filter elements. The filters were Teflon®-coated fiberglass felt rated for an operating temperature of up to 250 °C. An automated air pulse-back manifold similar to that on the HTF and product receiver filter was employed to clean the filter elements with the filters online. External electrical heaters maintained the filters and vessel above the gas dew point to prevent moisture condensation.

A sulfur-impregnated, granular-activated carbon (GAC) mercury adsorber was installed downstream of the process off-gas filter. The primary purpose of the GAC was to remove elemental mercury from the gas stream. The mercury adsorber consisted of a three-stage bed with off-gas sampling capability upstream and downstream of the adsorber. Final mercury analysis was performed in this stack downstream of the third stage. Ports were also provided to allow grab samples of the GAC solids. Figure 4.9 illustrates the process off-gas filter, one of three off-gas blowers, and the insulated mercury adsorber.

Figure 4.9. Hazen Process Off-Gas Filter, Off-Gas Blower, and Mercury Adsorber Systems (TTT and WGI 2007)

4.3.3 Radioactive Waste SRNL BSR System

FBSR has been demonstrated to be a viable technology for removing more than 99% of the organics and greater than 99% of the nitrate/nitrite from the SRNL Tank 48H simulant as well as forming a solid product that is primarily carbonate (Burket et al. 2008). The SRNL BSR was designed to demonstrate that the same product formation and off-gas reduction reactions would occur and that similar products would be formed when steam reforming actual radioactive Tank 48H waste. Comparisons of the simulated BSR waste product to that of the ESTD FBSR verified that the BSR was a viable option to emulate the chemistry of the ESTD FBSR Denitration Mineralization Reformer and CRR at the Hazen research facility.

The BSR designed and built at SRNL was a two-stage unit used to produce similar mineralized products and off-gases as simulated at the ESTD FBSR Tank 48H demonstration, but inside a shielded hot cell. A schematic of the unit flowsheet is illustrated in Figure 4.10.

The bench-scale reformer was designed and built to feed approximately 300 mL of feed slurry from an agitated seed vessel through a center feed port in the lid of the denitration mineralization reformer at a flow rate of about 1 mL/min. A solid carbonate product was formed in the DMR in the presence of saturated steam and carbon reductant, and the off-gases flowed through a condenser and bubbler to remove steam and particulate carryover on the way to a mass spectrometer before entering the CRR. The off-gases leaving the CRR received the same cooling and filtration treatment as the off-gas leaving the DMR before being piped to the same mass spectrometer.

The denitration mineralization reformer was designed with an inner reactor chamber of 70 mm inner diameter (ID) × 385 mm tall with a porous bottom. The bottom 75 mm of the reactor was filled with zirconia beads that were heavy enough not to be suspended by the gases and steam flowing up past them. The DMR outer chamber was 120 mm ID × 400 mm and housed the two 20-ft fluidizing-gas heating coils and connections for chamber pressure relief and feed lines. Water, CO_2, and air entered the DMR via the coil inlets and were converted to superheated steam and hot gases within the coil as a 1700-W furnace heated the outer shell of the DMR. The superheated steam and gases left the coils and flowed through the perforated bottom of the inner chamber, the zirconia beads, and the product, and out through the top of the DMR. The DMR inner reaction chamber could hold about 70 g of product, which was converted from about 300 mL of Tank 48H waste plus 60 g of Erwin coal reactants.

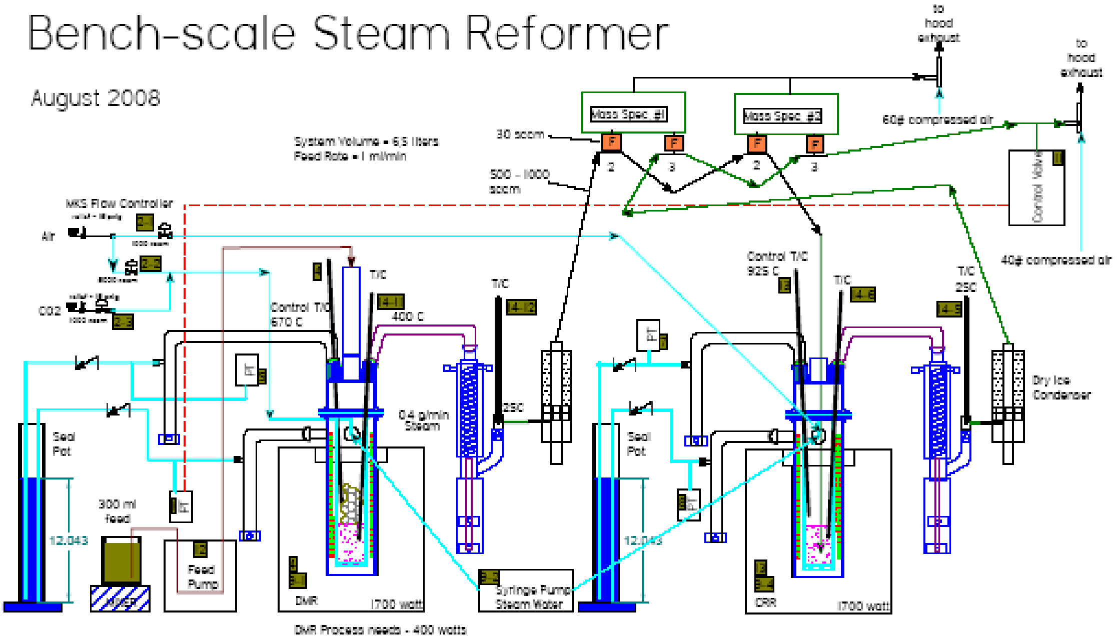

Figure 4.10. Schematic of the Bench-Scale Steam Reformer (from Burket et al 2008)

The waste feed was fed out of a 300-mL feed vessel and kept under constant agitation with the stir bar by means of a peristaltic pump to the top of the DMR where the feed was dripped onto the zirconia bead bed below. This feed contained ground and sifted (through an 80-mesh sieve) Erwin coal because space restrictions would not facilitate a separate feed of carbon reductant as is typical for pilot- or full-scale reforming operations.

Height restrictions within the shielded cell prevented the use of an FBSR because there would not be enough height to allow for proper disengagement of the product from the off-gas stream. This BSR was not fluidized, and the product formed was a porous stalagmite resting on top of the zirconia bead bed at the bottom of the DMR reactor chamber. Two Type K thermocouples positioned at 1.5 inches into the zirconia bead bed and 2 inches above the surface of the bead bed were used to verify the DMR operating temperature within the region of expected waste formation.

Off-gas from the DMR required pretreatment to prevent filter plugging or damage to the mass spectrometer. The off-gas first passed through a condenser that was chilled with water flowing at approximately 1 gpm and 5 °C. The off-gases and steam entered at the top of the condenser and flowed down through the center into a 75-mm-deep water reservoir filled with zirconia beads. Particulate matter that accumulates in the water and the gases would bubble up through the water and exit past the thermocouple and into a dry ice condenser. The dry ice condenser consisted of a 3-in.-ID × 9-in.-tall pipe with an inner 1-in.-ID tube for off-gas flow. Dry ice filled the space between the inner and outer pipes and typically froze out about 7 mL of liquid per test run. The dried off-gas stream was fed to two mass spectrometers to measure H_2, O_2, N_2, CO_2, benzene, and argon concentrations.

The CRR was similar in size and configuration to the DMR. Instead of having a feed line in the lid, it had a downcomer for the DMR off-gases to enter the chamber. The downcomer was a 13-mm-diameter tube that terminated 10 mm above the bottom of the inner chamber. The inner chamber was also filled with 75 mm of zirconia beads and as with the DMR, air and water flowed in through two 20-ft heating coils, inserted between the inner and outer chambers, to become hot air and superheated steam. This steam flowed up through the inner chamber and out through the lid. Thermocouples in the CRR were placed in similar locations to the DMR, and to control temperature, they were set to about 925 °C.

4.3.4 Studsvik BSSR[1]

The Studsvik BSSR is located at the Teledyne Brown Engineering Radiochemical Laboratory in Knoxville, Tennessee. It is a 2.4-in.-diameter quartz FBSR, a fully fluidized bed that produces both in-bed products and elutriated products. This unit is new. It has been operated with radioactive solid wastes and with simulated liquid sodium nitrate wastes. Because it is a fully fluidized FBSR that can operate in a continuous mode 24/7, it can produce larger quantities of in-bed and finer filter product solids for characterization and that allows the production of large-scale radioactive product solid monoliths and optimization of monolith binders up to ~5 gal monolith size. This unit can also be configured to operate with up to 6-in.-diameter quartz FBSR tubes.

Figure 4.11 is a photograph of the steam reformer submerged in the external electrical heating container. Figure 4.12 illustrates the BSSR positioned inside the insulated furnace. Three heating elements provide heating to the quartz BSSR.

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[1] Description derived from email correspondence. Brad Mason, *RE: FBSR Test Facilities*, May 6, 2010.

Figure 4.11. Photograph of Studsvik Bench-Scale FBSR[1]

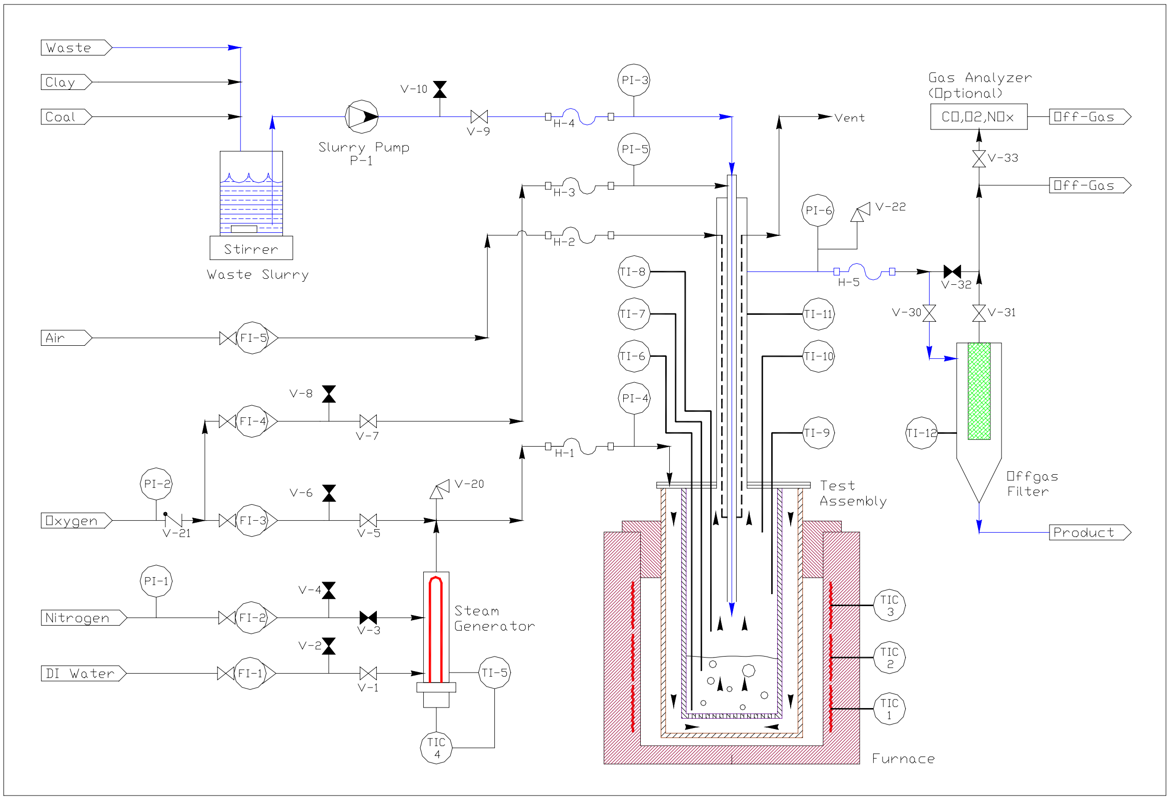

Figure 4.12. Studsvik FBSR Process Flow Diagram[1]

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[1] Courtesy Brad Mason, THOR Treatment Technologies, LLC.

5.0 Physical Properties

This section provides physical property data for the FBSR granular product and the FBSR granular product encapsulated in various binders. Data include density, particle size, and surface area for the FBSR granular product. Data are also provided on the density, surface area, and curing temperature for the FBSR monoliths.

5.1 FBSR Granular Product Physical Properties

This section provides information on the density, particle size, and surface area of the FBSR granular product.

Table 5.1 gives the density and surface area of the granular product from the early FBSR campaigns with INL SBW and the Hanford LAW campaign (Jantzen et al. 2006a). The measured Brunauer, Emmett, and Teller (BET) (1938)surface areas were measured in this study on a carbon-free basis (coal removed by roasting), and the value measured by McGrail et al. (2003c) (coal removed manually) was obtained for comparison. The geometric surface area is from Lorier et al. (2005).

Table 5.1. Density and Surface Area of FBSR Granular Products (from Jantzen et al. 2006a)

	Density by Pycnometry (g/cm^3)	Surface Area by BET (m^2/g)	Surface Area Geometric (m^2/g)
July 2003 SBW Campaigns			
Bed 260, 272, 277	3.30, 3.13, 2.73	6.03	
August 2004 LAW Campaigns			
Bed 1103	2.53	4.53	
Bed 1123	2.53	4.43	0.0212(a)
Fines 1125	2.46	4.41	
October 2004 SBW Campaigns			
Bed 1173	2.76	2.36	0.0194(a)
Hazen 2001 LAW Campaigns			
Bed SCT-02	2.66, 2.764(b)	2.37(b)	0.0193
PR-01 Fines	2.50	5.15	

(a) Lorier et al. (2005).
(b) McGrail et al. (2003c).

Figure 5.1 shows the particle size distribution for the HTF materials from the 2008 Hazen Research facility tests with the Hanford LAW and WTP-SW (secondary waste) waste simulants (TTT 2009). The HTF component was the major fraction of the FBSR product from these tests. HTF 5319 and 5379 are from the LAW simulant test, and HTF 5459 and 5514 are from the WTP-SW test. The distribution is generally bimodal at ~0.25 microns and ~30 microns. The clay additives are ~8 microns. Table 5.2 gives the bulk and particle densities for the HTF solids. The reader is referred to Figures 7.4 and 7.5 in the TTT report for the information on the particle size of the FBSR bed material.

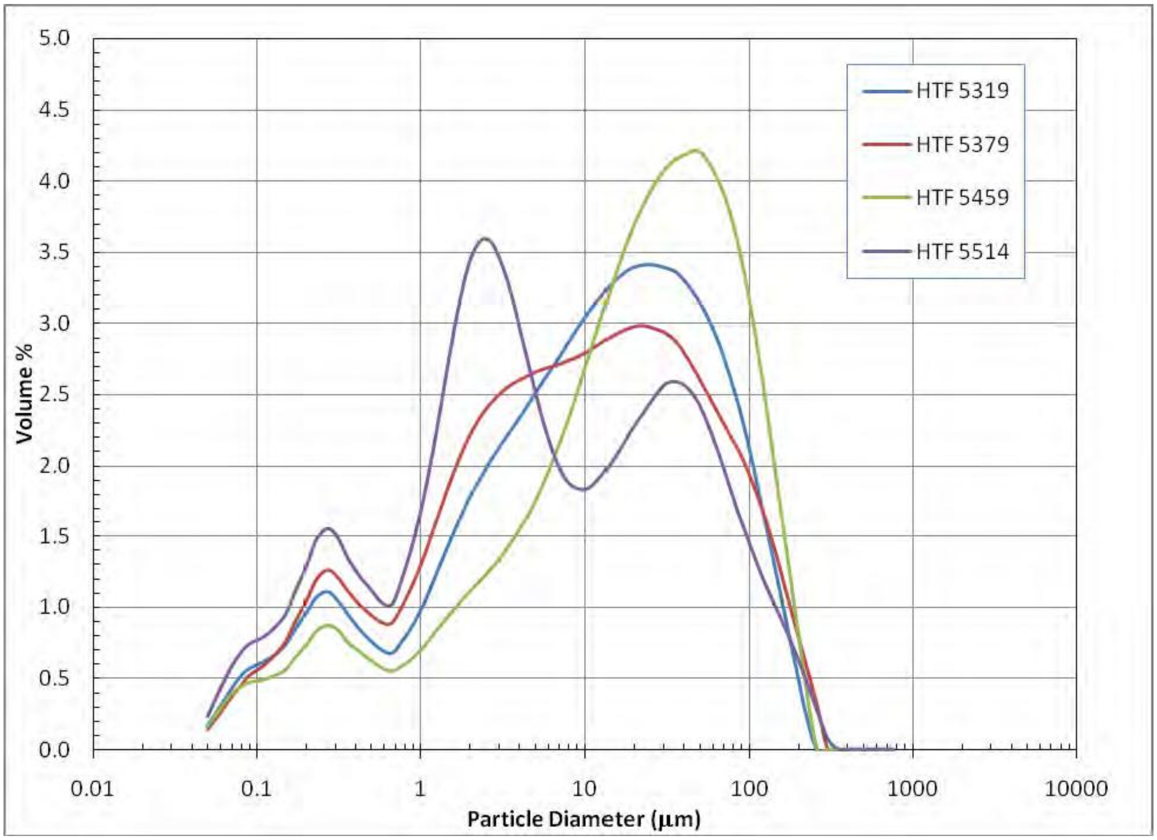

Figure 5.1. Particle Size Distribution for HTF Materials (from TTT 2009)

Table 5.2. Bulk and Particle Densities for HTF Materials (from TTT 2009)

Simulant	Sample ID	Bulk Density (g/cm^3) Loose	Bulk Density (g/cm^3) Packed	Particle Density (g/m^3)	Total Carbon (wt %)
LAW	5319	0.472	0.585	2.04	8.90
LAW	5379	0.492	0.673	2.13	1.26
WTP-SW	5459	0.485	0.576	1.68	20.7
WTP-SW	5514	0.722	0.898	2.92	3.43

5.2 FBSR Monolith Physical Properties

SRNL tested the durability of mineral waste forms that were produced between 2003 and 2004 in pilot-scale FBSR demonstrations at the SAIC STAR facility in Idaho. Material tested includes granular bed material from the DMR and the finer material from the filter (referred to in the report as the filter fines). Further information regarding products tested and preparation can be obtained from Jantzen (2006b). The FBSR material was solidified into monoliths using Type II Portland Cement, Ceramicrete, and hydroceramics. Table 5.3 shows the monoliths created from each material and the densities, waste loading, and compressive strength. Compression tests that were conducted on the monoliths used

ASTM C109-02 (cubes) for the cement and hydroceramic material and ASTM C39-04A (cylinders) for the Ceramicrete. Cure times were 7 days for the cement and hydroceramics and 14 days for the Ceramicrete with less than the 28 days typically used to show compliance with the 500-psi compressive strength requirement.

Table 5.3. Density and Waste Loading for FBSR Cement, Ceramicrete, and Hydroceramic Monoliths (from Jantzen 2006b)

Monolith	Density (g/cm^3)	Waste Loading (% dry basis)	Na_2O (wt%)	Compressive Strength (psi)
Cement Monoliths				
Cement A	1.68	84	17.53	890
Cement B	1.61	87	18.16	810
Cement C	1.72	80	16.70	1180
Cement D	1.38	80	16.70	2710
Cement E	1.18	81	16.90	250
Ceramicrete Monoliths				
SRNL	2.15	35.7		7100
ANL	2.14	35.7	7.45	4161
Hydroceramics Cured at 40ºC				
Hydroceramic A	1.56	50	10.44	76
Hydroceramic B	1.66	60	12.52	80
Hydroceramic C	1.80	80/83.3	16.70/17.39	106
Hydroceramics Cured at 70ºC				
Hydroceramic A-2	1.48	50		272
Hydroceramic B-2	1.53	60		320
Hydroceramic C-2	1.59	80		479
Hydroceramics Cured at 90ºC				
Hydroceramic A-3-a	1.50	50		80
Hydroceramic A-3-b	1.38	50		250
Hydroceramic B-3-a	1.50	60		710
Hydroceramic B-3-b	1.50	60		290
Hydroceramic C-3-a	1.61	83.3		1540
Hydroceramic C-3-b	1.78	83.3		820

To demonstrate FBSR technology, an ESTD was conducted at the Hazen Research facility. The ESTD demonstrates the THOR® FBSR technology in a full-scale unit (except the final product packaging). In 2008, mineralizing tests were conducted on Hanford LAW and WTP-SW wastes to demonstrate THOR® FBSR processes as a potential means to treat these waste types for disposal at the IDF. Two-inch cubes, 3- by 6-inch cylinders, and even larger 6- by 12-inch cylinder monolith samples were prepared from the LAW and WTP granular products. Measurements, including BET surface area, compressive strength, and density, were conducted on the different monolith samples, displayed in Table 5.4 (TTT 2009).

The heat of hydration isotherms was measured on the 6- by 12-inch cylindrical monolith samples over the duration of the cure time. Curing occurred in a humidity and temperature-controlled room at 23 °C. All monoliths displayed a less than 25 °C rise in temperature followed by a return to ambient temperature for approximately 10 hours. These results are displayed in Figure 5.2 (TTT 2009).

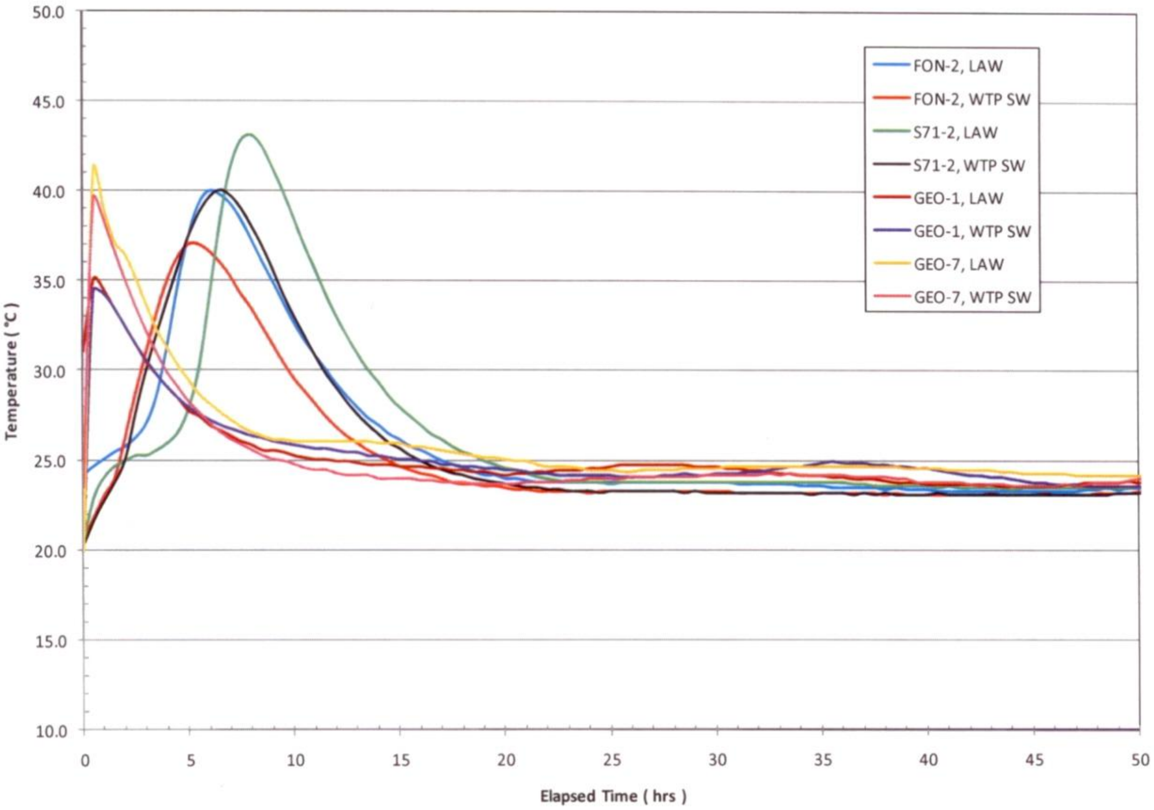

Figure 5.2. Heat of Hydration Isotherms Measured Over Cure Time for 6-inch Diameter by 12-inch Monoliths; Taken from TTT (2009)

Table 5.4. Compressive Strength, Density, and BET Surface Area Measurements FBSR Monoliths; Taken from TTT (2009)

	Size (inches)	Waste Loading	Cure Time (days)	Compressive Strength (psi)	Density	BET Surface Area (m^2/g)	Cure Time (days)	Compressive Strength (psi)	Density	BET Surface Area (m^2/g)
			Hanford LAW P-1B Solids				Hanford Off-Gas Recycle Secondary Waste			
Ordinary Portland Cement										
OPC-1	2×2×2	80%	12	1630	1.64	31.5				
OPC-2	2×2×2	87%	28	573	1.61	21.3				
High Alumina Cement										
FON-1	2×2×2	68%	7	770	1.77	20.0				
FON-2	2×2×2	74.16%	7	490	1.75	15.5				
	3d×6h	74.16%	28	580	1.69	15.5	18	570	1.68	30.83
	6d×12h	74.16%	28	370	1.69	15.5	28	420	1.67	30.83
S41-1	2×2×2	68.6%	7	672	1.75	10.7				
S41-2	2×2×2	74.16%	15	340	1.70	10.7				
S71-1	2×2×2	68.6%	7	1120	1.70	13.1				
S71-2	2×2×2	74.16%	15	550	1.65	9.2				
	3d×6h	74.16%	17	660	1.68	9.21	17	820	1.67	8.99
	6d×12h	74.16%	19	550	1.70	9.21	19	660	1.66	8.99
Geopolymers										
GEO-1	2×2×2	67%	11	1510	1.87	15.2				
	3d×6h	67%	14	1690	1.85	15.2	14	890	1.83	12.55
	6d×12h	67%	14	1530	1.82	15.2	19	1710	1.83	12.55
GEO-2	2×2×2	72%	14	860	1.87	17.3				
GEO-3	2×2×2	67%	11	1270	1.81	10.9				
GEO-4	2×2×2	71%	11	410	1.84	6.2				
GEO-5	2×2×2	63%	7	950	1.88	10.6				
GEO-6	2×2×2	66%	7	1080	1.82	10.0				
GEO-7	3d×6h	65.2%	14	2500	1.90	11.7	14	1980	1.83	26.86
	6d×12h	65.2%	18	1920	-	11.7	28	520	-	26.86
Ceramicrete										
CER-1	2×2×2	67%	8	520	1.81	32.2				
CER-2	2×2×2	73%	28	550	1.81	27.7				
NuCap										
NUCAP-1	2×2×2	45.5%	34	1250	1.44	0.09				

6.0 Waste Form Performance

The basis of the methods and protocols described in this section is the well constrained tests, i.e., tests in which variables are well controlled, and the test results have a well-known application. For most of these test protocols, the test results consist of determining the values of some parameters, which are subsequently included in equations that are ultimately used to calculate the release of elements of concern as a function of time and serve as a basis for the PA of a repository.

This is important because it is impossible to extrapolate test results from the longest laboratory tests, even those that have been ongoing for 25 years, to the times needed to demonstrate the safe disposal of nuclear waste. Equally, it is impossible to mimic a repository in laboratory settings and to conduct laboratory tests of different scales. Therefore, we should develop constitutive relationships that would allow us to calculate the behavior of a waste form over long time spans (preferably hundreds or thousands of years) and under a variety of conditions. In addition, the development of these constitutive relationships will allow us to design additional tests that more accurately target the values of the parameters in these equations, e.g., activation energy and the order of the reaction with respect to some solution species. And, perhaps as important as the parameter values, the uncertainties related to the parameter values should be also determined.

The following is a short description of different methods or standard procedures that are usually used to test waste form performance. In addition, a summary of the available data from the literature on tests conducted with the FBSR granular product and FBSR waste form (granular product encapsulated in a binder) is also provided below.

6.1 Leach Tests

The leaching tests are conducted on waste forms to evaluate their 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 dissolution behavior
- Generate data to determine the dominant release mechanism (reactions and kinetics) for each constituent of concern (COC)
- Provide a database for modeling the contaminant release from the waste forms over the life-span of a repository that may extend over thousands of years.

In this section, we will describe the second category of tests that have been conducted on FBSR waste forms and the results. The long-term performance of waste forms has been assessed using data from a number of test methods. These are the 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 2009d, Method 1316). If approved, these draft methods would replace the regulatory-based TCLP test (EPA 1992, Method 1311). The non-regulatory PCT and the EPA draft methods 1313 and 1316 have been used to assess the release of COCs from the FBSR waste forms. Following is a brief description of these methods and the results obtained. The description of regulatory tests and the results are discussed in the next section (Section 7, Waste Acceptance Criteria).

6.1.1 Waste Form Diffusivity

Several other test methods have been developed to measure diffusive releases while overcoming at least perceived deficiencies with the ANSI/ANS 16.1 method. Included in these methods are:

- ANSI/ANS 16.1, Measurement of the Leachability of Solidified Low-Level Radioactive Wastes by a Short-Term Test Procedure (ANS 2008)
- ASTM C 1308, Standard Test Method for Accelerated Leach Test for Diffusive Releases from Solidified Waste and a Computer Program to Model Diffusive, Factional Leaching from Cylindrical Waste Forms (ASTM 2008b)
- EPA Draft Method 1315, Mass Transfer Rates of Constituents in Monolithic or Compacted Granular Materials Using as Semi-Dynamic Tank Leaching Test (EPA 2009c)

The FBSR waste form encapsulated in the GEO-7 geopolymer has been tested with the EPA 1315 and ANSI/ANS 16.1 leach test methods.

6.1.1.1 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 (DI) water at a fixed liquid, volume-to-solid, surface-area ratio. The sampling is done at fixed periods of time. 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.

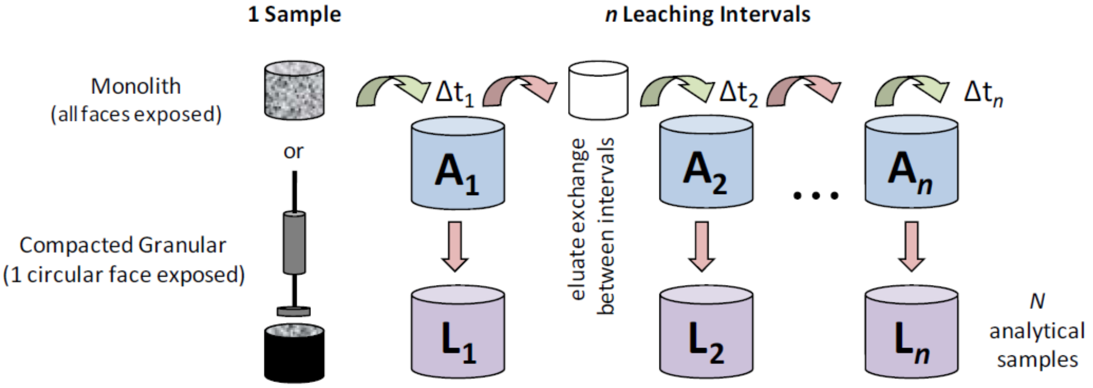

Figure 6.1. EPA 1315 Testing Scheme (EPA 2009c)

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 (ANS 2008), 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.

In this test, a cylindrical monolith sample (2-inch diameter by 4-inch height) is placed into the center of a leaching vessel containing DI water to maintain a solid-to-solution ratio of 9 ±1 mL of leachant per cm^2 of sample. A sample holder is 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 is calculated using the analytical solution, Equation 6.1, for simple radial diffusion from a cylinder into an infinite bath as presented by Crank (1986).

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

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_0 = 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)

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

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 the Hanford SW granular product encapsulated in the geopolymer binder are tabulated in Table 6.1. The test was extended beyond 63 days to obtain longer term waste form performance data.

Table 6.1. The Diffusivity and LI for Re and Na in Eluate for FBSR Waste Form from EPA Method 1315 (Pires et al. 2011)

Cumulative Leach Time (days)	Re Diffusivity (cm^2/s)	LI	Na Diffusivity (cm^2/s)	LI
0.08	6.44E-10	9.2	2.08E-08	7.7
0.08	1.46E-09	8.8	3.58E-08	7.4
1	4.82E-09	8.3	7.45E-08	7.1
1	4.85E-09	8.3	5.65E-08	7.2
2	1.75E-09	8.8	1.51E-08	7.8
2	2.08E-09	8.7	1.57E-08	7.8
7	5.63E-09	8.2	3.99E-08	7.4
7	5.46E-09	8.3	5.13E-08	7.3
14	5.58E-09	8.3	4.26E-08	7.4
14	4.87E-09	8.3	4.91E-08	7.3
28	3.25E-09	8.5	2.80E-08	7.6
28	2.86E-09	8.5	2.62E-08	7.6
42	1.14E-09	8.9	1.22E-08	7.9
42	1.12E-09	8.9	1.08E-08	8.0
49	5.05E-10	9.3	6.17E-09	8.2
49	5.34E-10	9.3	6.04E-09	8.2
63	2.61E-10	9.6	1.63E-09	8.8
63	2.69E-10	9.6	1.59E-09	8.8
149	1.84E-11	10.7	6.04E-11	10.2
189	2.23E-11	10.7	7.83E-11	10.1
222	1.67E-11	10.8	4.69E-11	10.3
306	9.96E-12	11.0	1.97E-11	10.7

6.1.1.2 ANSI/ANS 16.1

The ANSI/ANS 16.1 leach test method, Measurement of the Leachability of Solidified Low-Level Radioactive Wastes by a Short-Term Test Procedure (ANS 2008), has typically been used to characterize the leaching of radioactive constituents in LLW form. The ANSI/ANS 16.1 test was developed and used principally for cementitious materials, e.g., grouts, cements, and concretes. It is a test in which a monolithic test specimen is immersed in water and periodically removed from the solution and placed in a fresh solution. The method is similar to the EPA 1315 method. The leachant volume is 10× the geometric surface area of the sample, and the leachate samples are collected at 0.083, 0.29, 1, 2, 3, 4, 5, 19, 47, and 90 days. The NRC calls for this test method in their Technical Position on Waste Form (NRC 1991). Figure 6.2 shows the results of the ANSI/ANS 16.1 and EPA 1315 tests for the FBSR/GEO-7 monoliths.

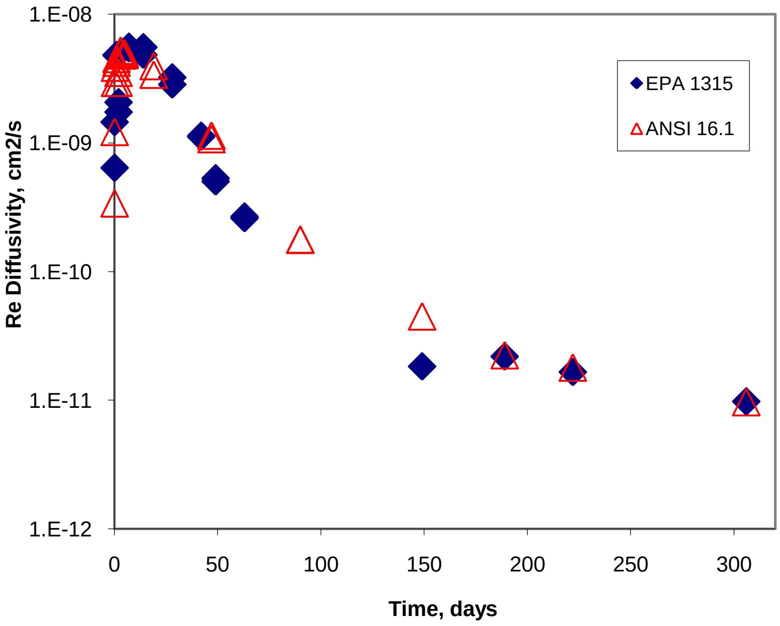

Figure 6.2. Diffusivity of Re in FBSR Monolith Waste Form for EPA Method 1315 and ANSI/ANS 16.1(from Pires et al. 2011)

6.1.2 Product Consistency Test

The PCT [ASTM C1285-02(2008)] (ASTM 2008a) was developed for checking the consistency of the glass produced at the Defense Waste Processing Facility at the Savannah River Plant in Aiken, SC. In the ASTM protocol, the vessel remains static. The test is performed with a surface-to-volume ratio (S/V) of 2000 m^{-1} at 90°C for 7 days (Part A), although other conditions can be used with Part B of the protocol.

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 = geometric surface area of the final waste form divided by the leachate volume, m^2/L.

Figure 6.3 shows the components of the PCT vessel (from Russell et al. 2006).

Figure 6.3. A Picture of Disassembled PCT Vessel (Russell et al. 2006)

This protocol has been used at SRNL and is covered in several articles and reports published by Jantzen and her collaborators (Jantzen 2004, , 2006a, b, 2007, 2008; Jantzen et al. 2004; 2005a, b; Lorier et al. 2005; Pareizs et al. 2005; Crawford and Jantzen 2007). The PCT has been conducted on both the granular FBSR product and on the FBSR product encapsulated in various binders. Table 6.2 lists PCT results (BET surface area) for the PR and the HTF FBSR product components from the 2008 Hazen ESTD tests using the Hanford LAW and LAW melter off-gas recycle stream (Hanford SW) simulants (Vora et al. 2009).

Table 6.3 lists the average PCT results for various binders using a blend of LAW and SBW FBSR granular product (Jantzen 2006b). The reader is referred to Figure 10-11 in the TTT (2009) report that shows PCT results (BET surface area) for LAW and Hanford SW simulants encapsulated in various binders (TTT 2009).

Table 6.2. Average PCT Results for LAW and Hanford SW FBSR Products (from Vora et al. 2009)

	Normalized Release (g/m^2)							
FBSR Product	Al	B	Cs	K	Na	Re	S	Si
LAW PR	0.0019	n/a	0.014	0.0003	0.013	0.0068	0.106	0.0006
LAW HTF	0.0021	n/a	0.0075	0.0002	0.015	0.024	0.188	0.0005
Hanford SW PR	0.0037	0.17	0.017	0.0001	0.013	0.007	0.076	0.0002
Hanford SW HTF	0.0031	0.09	0.013	0.0001	0.014	0.019	0.149	0.0001
LAW Reference					0.54			0.16

Jantzen and Crawford (2010) report that the FBSR granular product and monolith products are ~1 order of magnitude more durable than glass in the PCT if the BET surface area is used. If the geometric surface area is used, the durability of the two waste forms is approximately equivalent. They provide results based on both the geometric and BET surface area because the geometric surface area tends to underestimate the reactive surface area while the BET surface area tends to overestimate the reactive surface area (Pierce 2007).

Table 6.3. Average PCT Results for Various Binder Monoliths (10^{-3} g/m^2) (Jantzen 2006b)

Monolith	pH	Al	Cs	Na	Re	S	Si
Cement A	12.1	5.82	119	146	420	2.76	1.62
Cement B	12.2	5.68	136	163	382	4.48	1.03
Cement C	12.23	3.71	93.4	97.6	212	2.09	0.953
Cement D	12.21	296	7040	7250	19900	123	49.8
Cement E	12.29	1.78	30.5	70.5	206	3.11	0.974
Ceramicrete	11.61	0.247	76.6	85.7	185	6.55	0.772
Hydroceramic A	10.11	13.7	8.8	198	297	34.2	2.29
Hydroceramic B	11.04	10.1	9.41	161	132	29.6	3.74
Hydroceramic C	11.19	6.49	44.9	224	329	46.1	13.6

6.1.3 Effect of Leachant pH—EPA 1313 Leach Test

The EPA draft Method 1313 (Liquid-Solid Partitioning as a Function of Extract pH) is a static test method in which a set of parallel extraction experiments are conducted in dilute acid or base at a fixed pH (pH range from 4 to 12) and fixed liquid-to-solid ratio (10 mL/g) (EPA 2009a).

Before initiating the static test, a series of pre-titrations are 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 is centrifuged, the supernatant is removed, and it is used to determine the equilibrated pH. The powdered FBSR monolith material forms a high-alkaline solution after equilibrating in DI water for 24 hours, and therefore all pre-titrations and EPA 1313 leach tests were performed only with acid addition to the desired pH.

Based upon the pre-titration results, FBSR test samples were prepared by mixing 10 g of <0.3-mm sized material with a predetermined amount of 2 M HNO_3 and bringing the samples to volume with DI water. All samples were placed on a platform shaker and allowed to mix at room temperature (23 ± 2 °C) for 24 hours.

The measured concentrations of the major cations in the crushed FBSR monolith material (FBSR granular product in GEO-7 binder) leached at various pH solutions are shown in Table 6.4 (Pires et al. 2011). The concentrations increased as the leach solution pH decreased (became more acidic). Table 6.5 shows the concentrations of the detected RCRA metals, iodine, and rhenium in the leachates.

6.1.4 Effect of Liquid-to-Solid Ratio—EPA Method 1316 Leach Test

Similar to 1313, EPA Method 1316 (EPA 2009d) also is a static test method in which DI water is used as the leachant at a variety of liquid-to-solid ratios instead of a dilute acid or base (EPA 2009a). The purpose of this test method is to evaluate the effect of differing liquid-to-solid ratios on the release of contaminants. These experiments are conducted by adding DI water to the test vessel containing a predetermined amount of powdered material (<0.3 mm). With the FBSR materials, 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, the slurry samples were centrifuged, and the resulting clear supernatants were filtered through a syringe filter (0.45-µm pore size polypropylene membrane). The filtrate was collected in vials with minimal head space and submitted for chemical analyses.

Table 6.4. The Concentrations of Major Cations in Eluate for the FBSR Waste Form from EPA Method 1313 (Pires et al. 2011)

pH	Na (mg/L)	K (mg/L)	Al (mg/L)	Si (mg/L)	S (mg/L)	Fe (mg/L)
12.2	4820	62.4	ND	95.5	70.7	1.34
12.2	5130	66.4	ND	114	73.4	1.52
5.89	8170	123	10.4	60.2	119	ND
5.99	8150	124	9.86	57.9	118	ND
4.08	11200	276	240	138	93.5	2.1
3.97	11000	273	297	149	98.3	4.94
3.33	12100	343	2130	246	116	34.1
3.33	12200	348	2130	227	111	36.6

Table 6.5. The Concentrations of Select RCRA Metals, Iodine, and Rhenium in Eluate for the FBSR Waste Form from EPA Method 1313 (Pires et al. 2011)

pH	Cd (µg/L)	Cr (µg/L)	Pb (µg/L)	Hg (µg/L)	I (µg/L)	Re (µg/L)
12.2	35.2	55.7	21.5	43.2	1290	3410
12.2	36.2	56.3	22.4	43.7	1300	3500
5.89	50.3	238	ND	6.15	2270	10300
5.99	46.5	ND	ND	6.07	2100	10100
4.08	3720	ND	107	ND	993	17300
3.97	3620	ND	115	ND	1330	17300
3.33	7110	ND	778	ND	365	19700
3.33	6980	ND	775	ND	353	20000

ND indicates “not detected” below quantification level for Cr<9.58 µg/L; Pb<4.66 µg/L; Hg<1.81 µg/L.

The results of the EPA 1316 test are listed in Table 6.6 for the major cations and Table 6.7 for the RCRA metals, iodine, and rhenium from the crushed FBSR granular product in GEO-7 binder (Pires et al. 2011). The pH of the leachate solutions was between 12.5 and 12.8 for all three liquid-to-solid (L/S) ratios. In general, the concentrations of the cations, including the RCRA metals, showed higher concentrations in the leachates as the liquid-to-solid ratio decreased.

Table 6.6. The Concentrations of Major Cations in Eluate for the FBSR Waste Form from EPA Method 1316 (Pires et al. 2011)

L/S Ratio (mL/g)	Na (mg/L)	K (mg/L)	Al (mg/L)	Si (mg/L)	S (mg/L)	Fe (mg/L)
10	4650	66.9	5.61	320	69.7	6.50
10	4730	67.7	2.85	144	68.0	4.92
5	8800	129	7.51	1920	138	7.17
5	8840	128	8.72	1990	140	2.62
2	22300	326	54.0	8390	344	23.2
2	22400	334	68.4	8430	360	21.3

Table 6.7. The Concentrations of Select RCRA Metals, Iodine and Rhenium in Eluate for the FBSR Waste Form from EPA Method 1316 (Pires et al . 2011)

L/S Ratio (mL/g)	Cd (µg/L)	Cr (µg/L)	Pb (µg/L)	Ag (µg/L)	Hg (µg/L)	I (µg/L)	Re (µg/L)
10	97	101	94.2	52	47.3	1390	2730
10	89.1	93.5	84.2	11.6	48.6	1280	2710
5	103	114	164	3.23	100	1940	5430
5	106	117	177	ND	98.6	1940	5440
2	271	248	1120	ND	233	3980	13600
2	258	246	1090	ND	235	4060	13200

ND indicates “not detected” below quantification level for Ag<3 µg/L.

6.1.5 Single-Pass Flow-Through Test

The SPFT was developed at PNNL by McGrail (McGrail and Peeler 1995; McGrail et al. 1997b) and has been formalized as an ASTM procedure (ASTM 2010a). In the current version of this test, a powder or monolithic specimen is in contact with a flowing leachant. To determine the forward reaction rate, it is necessary to perform tests at a fast enough flow rate (q) and a low enough surface area (S) that the dissolution rate is independent of q/S. Experiments are then run to determine the effect of pH and other conditions on the dissolution rate. This test is used to determine rate law parameters.

This test has been used to determine the forward dissolution rate of an FBSR material at SRNL (Lorier et al. 2005; Jantzen et al. 2006a, 2007a) and PNNL (McGrail et al. 2003b). The results are reported with BET surface areas taken into account. The forward dissolution rates are generally on the order of 0.01 g/(m^2·d). The dissolution rate is expected to slow significantly as the water flow rate decreases. The dissolution of the material is, however, complex, the surface areas notwithstanding.

Because the FBSR material is composed of at least three major minerals (nosean, sodalite, and nepheline), it is unclear which of these minerals is dissolving with the highest rate and how the dissolution of the relatively less stable mineral phase affects the dissolution of the other more stable mineral phases. This is yet to be determined. In addition, the affinity of these different mineral phases for Re or Tc and the location of Re or Tc within the mineral crystal structures is still uncertain.

McGrail et al. (2003b) performed several experiments with FBSR materials in which the q/S ratio was varied to find the flow-rate independent conditions. They determined that this occurred at a flow rate of 140 mL/d or a q/S of 1.4×10^{-9} m/s. Lorier et al. (2005) used four temperatures, 25 °C, 40 °C, 70 °C and 90 °C and five buffer solutions for 14–16 days. They used 1 gram[1] of specimen in their tests. In their experiments, they used a flow rate of 288 mL/d, suggesting that more than 0.5 g of specimen had been added to their tests. The BET surface areas for the test specimens were equal to or 2 times greater than those used by McGrail et al. (2003b).

McGrail et al. (2003b) also performed the SPFT tests for 40 days at 25°C and 40°C because it took longer to achieve a steady state from which accurate rate data may be obtained. At 70°C and 90°C, a steady state was achieved much sooner, so the tests were run for 21 to 24 days.

6.1.6 Pressurized Unsaturated Flow Test

The PUF test (McGrail et al. 1997a, 1999a) was developed initially to mimic the unsaturated conditions that exist in the IDF at Hanford, where the LAW glass is to be disposed of (Mann et al. 1998). However, it has proven much more useful.

The reactions that normally occur over very long times in standard tests, such as the ASTM C1285-02(2008) test (ASTM 2008a) (PCT) or the ASTM C1220-10 protocol (ASTM 2010b) (Materials Characterization Center [MCC]-1)(MCC 1981), occur quite rapidly in this test. It is a dynamic column test in which the test specimen or test specimen configuration (McGrail et al. 1999b) is kept in contact with water under unsaturated conditions, i.e., the water only flows on the surface of the specimen particles and does not entirely fill the pores. Unsaturated conditions are maintained by pressurizing the inside of the column to a pressure just below the capillary pressure of a sintered metal disk at the bottom of the column. Since the capillary pressure of the disk is greater than that of the specimen column, the water column can only be maintained at the near surface of the metal disk. The atmosphere in the column can be maintained with the external gas that is used to pressurize the column. Temperatures up to 90°C have been used, although much higher temperatures are theoretically possible.

The PUF test has been performed at PNNL on an FBSR material (Pierce 2007). The results appear to be consistent with results from the SPFT test (Pierce 2007). However, the results from this test are incomplete because the outlet of the test apparatus plugged from fines from the test media, eventually terminating the test before a complete data set could be obtained (Pierce 2007). Nevertheless, the initial results suggested that the FBSR product dissolved at a rate about 10 times lower than an LAW glass based on the BET surface area to account for the surface roughness. If the geometric surface areas were used rather than those determined with the BET method, the dissolution rates would have been comparable to about 10 times higher than the LAW glass.

6.2 Contaminant Release Mechanisms

Jantzen (2008) prepared a summary of current knowledge regarding the mineralization of radioactive wastes by the FBSR process and a comparison of the durability glass and the FBSR mineral phases. The following excerpt is from the executive summary of that document.

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[1] Personal communication from Carol Jantzen and Eric Pierce.

The Savannah River National Laboratory (SRNL) was requested to generate a document for the Washington State Department of Ecology and the U.S. Environmental Protection Agency that would cover the following topics:

- *A description of the mineral structures produced by Fluidized Bed Steam Reforming (FBSR) of Hanford type Low Activity Waste (LAW) waste, especially the cage structured minerals and how they are formed.*
- *How the mineral cage structured minerals contain some contaminants, while others become part of the basic mineral structure.*
- *Possible contaminant release mechanisms from the mineral structures.*
- *Appropriate analyses to evaluate these release mechanisms.*
- *Why the appropriate analyses are comparable to the existing Hanford glass dataset.*

Mineral waste forms, which include mineral assemblages formed by FBSR, those formed by Hot Isostatic Pressing (HIPing) such as SYNthetic ROCk (SYNROC), Hot Uniaxial Pressing (HUPing), and those formed by Cold Uniaxial Pressing (CUPing) and sintering (SYNROC, supercalcine ceramics, tailored ceramics, and Pu ceramics) possess what are referred to as short range order (SRO), medium range order (MRO), and long range order (LRO). The SRO has a radius of influence ~1.6-3Å around a central atom or first nearest neighboring atoms, the medium-range order has a radius of influence ~3-6 Å which encompasses second and third-nearest neighbor environments around a central atom, and the long range order extends beyond third-neighbor environments and gives the crystalline mineral structures their crystallographic periodicity.

In the sodium aluminosilicate (NAS) FBSR mineral structures, the contaminants in the cage-shaped structures and those external to the cage like structures are all bound ionically to oxygen atoms. The NAS minerals form from the sodium in the LAW waste and a processing additive (kaolin clay), which provides the SiO_2 *and* Al_2O_3*. Other mineral phases containing phosphate, boron, iron, and other alkali or alkaline earth elements could form depending on the waste composition and the process additives. The NAS cage structured feldspathoid minerals such as sodalite, nosean, and nepheline, which are common to FBSR and supercalcine ceramic waste forms, are formed by SRO and MRO structures* $(SiO_4)^{-4}$ *and* $(AlO_4)^{-5}$ *tetrahedra), which are joined by sharing one or more of the four oxygen atoms with another tetrahedra; the linking oxygens are known as bridging oxygen bonds. The tetrahedral are arranged to form a cage (sodalite, nosean) or rings (nepheline) via one or two of the tetrahedral oxygen atoms, while the other tetrahedral oxygen atoms (known as non-bridging oxygens) are available to bond ionically with the cations in the cage or outside the cage. These cations may be alkali, alkaline earths, hazardous, or radioactive species. The cage and/or ring structures are repeated in the structure at regular periodicity, which is the LRO characteristic of mineral/crystalline structures. The LRO provides shorter and more regular oxygen-cation (ionic) bonding and a periodic ordering, which makes the contaminant retention in mineral/ceramic waste forms greater than glass.*

The NAS FBSR minerals are formed by destabilization of kaolin clay at the moderate processing temperature (700-750°C). In kaolin clay the aluminum atom is octahedrally coordinated (six nearest neighbors instead of four). The aluminum atom is surrounded by 2 oxygen atoms and four OH- atoms. During processing at 700-750°C, the four OH- atoms are vaporized, leaving the Al atoms in the clay unstable and amorphous at the nanoscale. The alkali in the waste reacts with the unstable Al atom and rearranges to a crystalline (mineral) lowest free energy tetrahedral configuration forming mineral species such as $NaAlSiO_4$.

Glasses do not possess LRO, but they do possess SRO and MRO. Some times glasses have more highly ordered regions, referred to as clusters or quasicrystals that have atomic arrangements that approach those of crystals, but no LRO. Experimentation has confirmed that glasses contain framework units, sheet-like units, chain-like units, and monomers made up of tetrahedra of $(SiO_4)^{-4}$, *boria as* $(BO_4)^{-5}$, $(PO_4)^{-3}$, $(AlO_4)^{-5}$, *or* $(BO_3)^{-3}$ *trigonal units. The competition for a dominant structural role causes one or more of the three types of* (SiO_4)*-4,* (BO_4)*-5,* (PO_4)*-3 tetrahedral units to phase separate, while* (AlO_4)*-5 tetrahedra inhibit phase separation. In borosilicate glasses, (PO4)-3 will separate first, along with accompanying charge balancing cations.*

If glasses contain $(SiO_4)^{-4}$, $(BO_4)^{-5}$, $(BO_3)^{-3}$ *and some* $(AlO_4)^{-5}$ *they are borosilicate glasses; if they contain* $(SiO_4)^{-4}$ *and* $(AlO_4)^{-5}$ *they are aluminosilicate glasses; if they contain only* $(BO_4)^{-5}$, $(BO_3)^{-3}$ *and some* $(AlO_4)^{-5}$ *they are aluminoborate glasses; and if they contain* $(PO_4)^{-3}$ *and* $(AlO_4)^{-5}$ *they are aluminophosphate glasses and so on. Glasses are metastable compared to crystalline minerals because crystalline species are at their lowest thermodynamic free energy. Glasses do not have LRO and thus NAS FBSR mineral structure waste forms are inherently more stable and tend to be as durable or more durable than vitreous waste forms, depending on which elements are being monitored, i.e. SRO structural species such as Si and Al or cations that leach by ion exchange that are bonded to the oxygen cations of the SRO structures.*

Because of the similarity of the SRO and MRO in mineral (ceramic) and vitreous waste forms the dissolution mechanisms (contaminant release mechanisms) are similar. Mineral waste forms can afford better retention of cationic species compared to glass waste forms due to the LRO of the mineral structure and the regularity of the coordination and bonding of a given coordination polyhedra in which a cation or radionuclide resides. While the activation energy required to break an Si-O, Al-O, B-O bond may be similar in a glass and a ceramic/mineral due to the SRO, the $(SiO_4)^{-4}$, $(BO_4)^{-5}$, $(BO_3)^{-3}$ *and some* $(AlO_4)^{-5}$ *are more rigidly retained in a mineral structure due to the LRO and periodicity (repeated pattern) of the polyhedra.*

In mineral waste forms, as in glass, the molecular structure controls contaminant release by establishing the distribution of ion exchange sites, hydrolysis sites, and the access of water to those sites. It has been demonstrated experimentally that ion exchange in glass occurs along percolation channels that exist in glass. The percolation channels in glass are defined by the SRO and MRO structure of a given glass since glass has no LRO. The cations in the percolation channels are ionically bonded to the non-bridging oxygen (NBO) bonds, just as they are in the more ordered crystalline mineral species. In the *mineral waste forms there are no percolation channels and dissolution with water must attack the ionically bonded lattice from the surface. The basic difference is that there may be fewer bonds around a given cation in a glass or the bonds may have varying lengths compared to those in a crystalline or mineral waste form. Examples include: 1) The release of Na from crystalline nepheline is slower than that from a glass with the identical composition; 2) Ceramic Pu waste forms are more durable than vitreous Pu waste forms, and 3) Ceramics such as SYNROC and high Al Tailored Ceramics are more durable than borosilicate glass.*

The appropriate analyses for the determination of the release of contaminants from ceramics are the same as those for glass and the glass ceramic known as "glass bonded sodalite." Because the FBSR product is granular, certain monolithic tests like ASTM C1220 (MCC-1 described in the appendix) cannot be performed unless the granular product is monolithed. However, the standard suite of durability tests applicable to both granular or ground up monolithic waste forms, i.e. the Product Consistency Test (PCT or ASTM C1285), the Single Pass Flowthrough Test (SPFT or ASTM C1662), and the Pressure Unsaturated Flowthrough (PUF) test, provide the different parameters necessary for an understanding of the durability of one waste form compared to the other and/or the mechanisms by which a waste form degrades.

In most studies, the PCT is used to determine the maximum rate of radionuclide release if the leaching is congruent (i.e., the release rate of contaminants is essentially the same as the release of Na) and the SPFT test is used to monitor the rate of matrix degradation. It should also be noted that the SPFT test originated for the geologic study of the degradation of single phase minerals in nature, but there are consistency issues between laboratory studies regarding the manner in which surface areas of the waste forms are measured and in the choice of buffer solutions for performing the tests. The consensus has been to use geometric surface area for smooth surface waste forms (glasses and glass ceramics) and Brunauer-Emmett-Teller (BET) surface area for ceramic and mineral waste forms to account for surface roughness. If the leach rates of the FBSR mineral product are expressed conservatively, i.e. without the SA term, then glass and FBSR product have similar durability. If the leach rates of the FBSR product are expressed with the surface roughness term which is much greater than the surface roughness of glass, then the FBSR product is two orders of magnitude more durable than glass.

The durability testing (PCT, ASTM C1285) on the FBSR mineral waste form has shown that an Al-buffering mechanism controls the release of alkali (Na, K, and Cs) elements and the solution pH controls the release of the other constituents like Re (simulant for Tc99), S, and Si. This is due to the high alumina content of the FBSR mineral products, which provides a natural aluminosilicate buffering mechanism that inhibits leaching. This mechanism is known to occur in nature during weathering of aluminosilicate mineral analogs. Since glasses do not normally contain high alumina contents (high alumina glasses are too viscous to process), such an aluminosilicate buffering mechanism has not been observed for glass waste forms. In glass Na, B, and Li releases are congruent with the maximum radionuclide release rate, which happens to be the element Tc^{99}*. Because ceramics normally leach incongruently, the leach rates of Re (surrogate for* Tc^{99}*) from the NAS FBSR mineral phases should be compared to the leach* *rates of Na or B from LAW glass, i.e. the release of B from the LAW glass standard known as Low Activity Reference Material (LRM) during PCT testing is 0.55 g/m^2, the Hanford PCT specification is 2 g/m^2, and the release of B from the AN-102 radioactive waste glass tested at SRNL is 0.29 g/m2. The Re release from the 2002 FBSR LAW (AN-107) product is 0.22-0.29 g/m^2, while the Cs release is 0.16 g/m^2. No correlation exists between the congruent Na release rates of LAW glass and the incongruent Na release from the FBSR LAW mineral waste form. The leachate buffering mechanism and the fact that the FBSR mineral product contains the radionuclides in a structure that has LRO makes the FBSR mineral products more durable than glass.*

Durability testing (SPFT and PUF) performed by the Pacific Northwest National Laboratory (PNNL) also indicates that the FBSR mineral product is more durable than LAW glass by ~ 2 orders of magnitude. Additional SPFT testing at SRNL demonstrated that all of the mineral species present in the FBSR product (nepheline, nosean, and sodalite) share the same bonding (SRO, MRO and LRO) in terms of the aluminosilicate matrix, i.e. a basic structural framework formula [AlSiO4-]6 that forms the rings and cages in which the radionuclides, halides, and sulfates are bonded. The SRNL durability data indicated that the structural framework leaches congruently and that the Re (Tc^{99}) and S cannot be released from the cage until part of the tetrahedral components of the cage themselves degrade. The reaction order for nepheline dissolution determined for the FBSR LAW mineral components (nepheline and sodalite) in the SRNL study agree with those measured on single crystal natural nepheline and with the data on glass bonded sodalite ceramic waste forms at comparable dissolution temperatures (80-90°C). The PNNL data is not in agreement with the data on natural nepheline and/or the data on glass bonded sodalites. However, the durability (as indicated by the reaction order) measured for the LAW FBSR mineral product by both SRNL and PNNL are lower than the reaction order measured on nepheline glass and on a simple five component High Level Waste glass at similar dissolution temperatures. This data again demonstrates that the FBSR product is more durable than glass since SPFT testing includes the exposed surface area of the waste form.

End of citation (Jantzen 2008).

7.0 Waste Acceptance Criteria

7.1 Void Space

Methods to consolidate the FBSR granular product into monolith waste forms are being investigated (Jantzen 2007; TTT 2009). The porosity and void volume of these materials on an engineering or production scale are, as yet, unknown.

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 the 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 waste streams from WTP, DB3, supplemental treatment using bulk vitrification, and Basin 42. The highest dose rate was from radionuclides in the DB3 waste stream. A 4-ft × 4-ft × 4-ft concrete block with a specific density of 1.5 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. 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.

The ETF will not accept wastes for treatment with radionuclide concentrations above its design basis and administrative controls. Wastes treated and solidified in ETF will not exceed the IDF dose rate limits.

7.3 Free Liquids

Because the steam reforming process involves high-temperature steam, no free liquids are expected in the granular product. During a process upset, free liquids might be present, but these “off-spec” materials could be recycled to the steam reformer. Any free liquids would be introduced through the encapsulation process. Cements, geopolymers, hydroceramics, and Ceramicrete all require water for the solidification process. These processes can be controlled to minimize/eliminate free liquids.

7.4 Dangerous Waste Limitations

A few TCLP (EPA 1992) tests have been performed on FBSR granular product (Jantzen 2002; Jantzen et al. 2005a,b; Crawford and Jantzen 2007; TTT 2009). Table 7.1 shows the results for TCLP tests on various FBSR granular products from LAW, WTP-SW, and SBW tests. Except for chromium in the 2004 SBW and LAW STAR FBSR tests and cadmium and antimony in the 2008 Hazen LAW and WTP-SW tests, the FBSR granular product passed the TCLP based on the Universal Treatment Standards in 40 CFR 268. Pareizs et al. (2005) observed that the 2004 SBW and LAW STAR tests did not include magnetite and therefore the chromium was not sequestered in the magnetite spinel phase observed when magnetite is used. As discussed in the next paragraph, in the 2008 Hazen tests, cadmium and antimony were spiked by factors of at least 10 their expected concentrations in the LAW and WTP-SW wastes. At their expected concentrations in the wastes, they are expected to pass the TCLP.

TCLP tests were performed FBSR waste form monolith specimens made with material from engineering-scale steam reformer runs and LAW and WTP secondary waste (TTT 2009). In the LAW tests, the target concentrations for Sb, As, Ag, Cd, and Tl increased by a factor of 10 and Ba was increased by a factor of 100 above their nominal concentrations to improve detection through the process tests. Similarly, for the WTP-SW tests, the target concentrations for Ni and Pb were increased by a factor of 10, Ag was increased by a factor of 1000, Cd by a factor of 1297, Sb by a factor of 48, Se by a factor of 16 above their nominal concentrations. Barium and thallium concentrations were set above their nominal concentrations at 1000 times their analytical detection limits in the feed solution (TTT 2009). The results indicated that the FBSR monolith materials passed the TCLP test with concentrations less than the Universal Treatment Standard (UTS); however, the values for Cd, Sb, and Se were above the UTS without correction for some of the binder materials as shown in Table 7.2. A correction for the high concentrations of these elements in the simulated waste was made, and these values fell below the UTS (TTT 2009).

While the pH of the leachants from the FBSR material are in the range of 12 to 13 for static tests, such as the PCT (Crawford and Jantzen 2007), these are not considered hazardous, especially because the high pH would be partly mitigated by the Hanford soil and the presence of CO_2 (g) in the pore space of the vadose zone soil. Other than the local high pH values, these leachates are not corrosive.

7.5 Compressive Strength

Cements and geopolymers are being investigated for consolidating the FBSR product (TTT 2009). Typically cement or grout have sufficient compressive strength to meet current guidelines of 60 psi (400 kPa) for LLW and a higher specification of 500 psi has been set for cement based materials (NRC 1991). All of the candidate consolidated FBSR products meet this higher guideline.

Data from TTT (2009) are shown in Table 7.3. See also Tables 5.3 and 5.4. Data are not available regarding the impacts of radiation, biodegradation, and water immersion on the compressive strength of the FBSR granular product encapsulated in any of the binder materials being considered.

7.6 Leachability Index

See Section 6 for a discussion of the methods by which the LI is measured. For secondary wastes, LI targets have been established for sodium, technetium, and iodine with LIs greater than 6, 9, and 11, respectively, after 90 days (see Appendix B). These correspond to diffusivities of 1×10^{-6} cm^2/s for Na, 1×10^{-9} cm^2/s for Tc/Re, and 1×10^{-11} cm^2/s for I. The ANS-16.1 (ANS 2008) and EPA 1315 (EPA 2009c) diffusivity tests have been conducted on the WTP-SW FBSR granular product encapsulated in the GEO-7 geopolymer binder. The LI for sodium was better than their respective targets for the duration of the two test methods. For rhenium, the LI was better than its target after about 42 days of testing. Extending beyond 90 days, the rhenium LI continued to improve to better than 10 after 149 days.

Table 7.1. TCLP Results for FBSR Granular Product

	August 2004 LAW[a]		October 2004 SBW[a]	2006 Hazen SBW[b]	2002 Hazen LAW[c]	2008 Hazen[d]		
Element	Bed 1104 (mg/L)	Fines 1125 (mg/L)	Bed 1173 (mg/L)	Various	AN-107 (mg/L)	LAW P-1B (mg/L)	WTP-SW P-2B (mg/L)	Universal Treatment Standard (mg/L)[e]
RCRA Metals								
As	--[f]	--	--	--	--	Pass	Pass	5.0
Ba	0.069	0.17	<0.034	--	--	Pass	Pass	21
Cd	--	--	--	--	--	Above UTS	Pass	0.11
Cr	9.2	8.4	0.82	0.0-0.44	0.015-0.06	Pass	Pass	0.60
Pb	0.046	<0.031	<0.031	0.011-0.2	0.002-0.067	Pass	Pass	0.75
Se	--	--	--	--	--	Pass	Pass	5.7
Ag	--	--	--	--	--	Pass	Pass	0.14
Hg	--	--	--	<0.00086	--	--	--	0.025
Underlying Hazardous Constituents								
Sb	--	--	--	--	--	Above UTS	Above UTS	1.15
Be	--	--	--	--	--	--	--	1.22
Ni	--	--	--	0.0-0.37	0.001-3.11	Pass	Pass	77
Tl	--	--	--	--	--	Pass	Pass	0.20

(a) From Jantzen et al. (2005a,b).
(b) Crawford and Jantzen (2007).
(c) From Jantzen (2002).
(d) From TTT (2009).
(e) 40 CFR 268.
(f) Not present in waste simulant.

Table 7.2. TCLP Results for FBSR Monolith Materials[(a)]

		LAW Monoliths										WTP-SW Monoliths									
		RCRA Metals							UHC			RCRA Metals							UHC		
Binder	Size (inches)	As	Ba	Cd	Cr	Pb	Se	Ag	Sb	Ni	Tl	As	Ba	Cd	Cr	Pb	Se	Ag	Sb	Ni	Tl
OPC-1	2×2×2	P	P	P	P	P	P	P	P	P	P										
OPC-2	2×2×2	P	P	P	P	P	P	P	P	P	P										
FON-1	2×2×2	P	P	P	P	P	P	P	P	P	P										
FON-2	2×2×2	P	P	P	P	P	P	P	P	P	P										
	3d×6h	P	P	P	P	P	P	P	P	P	P	P	P	P	P	P	P	P	P	P	P
	6d×12h	P	P	P	P	P	P	P	P	P	P	P	P	P	P	P	P	P	P	P	P
S41-1	2×2×2	P	P	P	P	P	P	P	P	P	P										
S41-2	2×2×2	P	P	P	P	P	P	P	P	P	P										
S71-1	2×2×2	P	P	P	P	P	P	P	P	P	P										
S71-2	2×2×2	P	P	P	P	P	P	P	P	P	P										
	3d×6h	P	P	P	P	P	P	P	P	P	P	P	P	NO	P	P	NO	P	P	P	P
	6d×12h	P	P	NO	P	P	P	P	P	P	P	P	P	NO	P	P	P	P	P	P	P
GEO-1	2×2×2	P	P	NO	P	P	P	P	P	P	P										
	3d×6h	P	P	P	P	P	P	P	NO	P	P	P	P	P	P	P	P	P	NO	P	P
	6d×12h	P	P	P	P	P	P	P	P	P	P	P	P	P	P	P	P	P	NO	P	P
GEO-2	2×2×2	P	P	NO	P	P	P	P	P	P	P										
GEO-3	2×2×2	P	P	NO	P	P	P	P	NO	P	P										
GEO-4	2×2×2	P	P	P	P	P	P	P	NO	P	P										
GEO-5	2×2×2	P	P	P	P	P	P	P	NO	P	P										
GEO-6	2×2×2	P	P	P	P	P	P	P	NO	P	P										
GEO-7	3d×6h	P	P	NO	P	P	P	P	NO	P	P	P	P	P	P	P	P	P	P	P	P
	6d×12h	P	P	P	P	P	NO	P	P	P	P	P	P	P	P	P	NO	P	P	P	P
CER-1	2×2×2	P	P	P	P	P	P	P	NO	P	P										
CER-2	2×2×2	P	P	P	P	P	P	P	P	P	P										
NUCAP-1	2×2×2	P	P	NO	P	P	P	P	P	P	P										

(a) From TTT 2009. Specific leachate concentrations are not provided, just an indication whether or not the material met the UTS limits for that RCRA metal or underlying hazardous constituent (UHC). Mercury and beryllium were not included in the simulants and are not included in this table.

Table 7.3. Compressive Strength Data for FBSR Monoliths

Waste Form	Waste Type/ Loading	Actual Waste/ Simulant/Spikes	Preparation	Test Method	Compressive Strength, GPa	Reference
FON-2 (high alumina cement)	P-1B (LAW) 74.2 mass%	Simulant/Re, I, Cr, Ag, Cd, Pb, Sb, Tl	As prepared	ASTM-C109/C109M (ASTM 2008c) ASTM-C39/C39M-99 (ASTM 1999)	3.4 (50 mm cube; 7 d cure) 4.0 (75 mm d × 150 mm h; 28 d cure) 2.6 (150 mm d × 300 mm h; 28 d cure)	TTT (2009)
S71-2 (high alumina cement)/	P-1B (LAW) 74.2 mass%	Simulant/Re, I, Cr, Ag, Cd, Pb, Sb, Tl	As prepared	ASTM-C109/C109M (ASTM 2008c) ASTM-C39/C39M-99 (ASTM 1999)	3.8 (50 mm cube; 15 d cure) 4.6 (75 mm d × 150 mm h; 17 d cure) 3.8 (150 mm d × 300 mm h; 19 d cure)	TTT (2009)
GEO-1 (geo-polymer)	P-1B (LAW) 67 mass%	Simulant/Re, I, Cr, Ag, Cd, Pb, Sb, Tl	As prepared	ASTM-C109/C109M (ASTM 2008c) ASTM-C39/C39M-99 (ASTM 1999)	10.4 (50 mm cube; 11 d cure) 11.7 (75 mm d × 150 mm h; 14 d cure) 10.5 (150 mm d × 300 mm h; 14 d cure)	TTT (2009)
GEO-7 (geo-polymer)	P-1B (LAW) 74.2 mass%	Simulant/Re, I, Cr, Ag, Cd, Pb, Sb, Tl	As prepared	ASTM-C109/C109M (ASTM 2008c) ASTM-C39/C39M-99 (ASTM 1999)	17.2 (75 mm d × 150 mm h; 14 d cure) 13.2 (150 mm d × 300 mm h; 18 d cure)	TTT (2009)
FON-2 (high alumina cement)	P-2B (WTP-SW) 74.2 mass%	Simulant/Re, I, Cr, Ag, Cd, Pb, Sb, Tl	As prepared	ASTM-C39/C39M-99 (ASTM 1999)	3.9 (75 mm d × 150 mm h; 18 d cure) 2.9 (150 mm d × 300 mm h; 28 d cure)	TTT (2009)
S71-2 (high alumina cement)	P-2B (WTP-SW) 74.2 mass%	Simulant/Re, I, Cr, Ag, Cd, Pb, Sb, Tl	As prepared	ASTM-C39/C39M-99 (ASTM 1999)	5.7 (75 mm d × 150 mm h; 17 d cure) 4.6 (150 mm d × 300 mm h; 19 d cure)	TTT (2009)
GEO-1 (geo-polymer)	P-2B (WTP-SW) 74.2 mass%	Simulant/Re, I, Cr, Ag, Cd, Pb, Sb, Tl	As prepared	ASTM-C39/C39M-99 (ASTM 1999)	6.1 (75 mm d × 150 mm h; 14 d cure) 11.8 (150 mm d × 300 mm h; 19 d cure)	TTT (2009)
GEO-7 (geo-polymer)	P-2B (WTP-SW) 74.2 mass%	Simulant/Re, I, Cr, Ag, Cd, Pb, Sb, Tl	As prepared	ASTM-C39/C39M-99 (ASTM 1999)	13.7 (75 mm d × 150 mm h; 14 d cure) 3.6 (150 mm d × 300 mm h; 28 d cure)	TTT (2009)

8.0 Summary of Key Waste Form Attributes

The primary product from the FBSR process is a granular product composed of sodium aluminosilicate minerals. The sodium aluminosilicate FBSR granular product is a multiphase mineral assemblage of Na-Al-Si (NAS) feldspathoid minerals (sodalite, nosean, and nepheline) with cage and ring structures that sequester anions and cations (Jantzen et al. 2007b). Nepheline is the basic sodium aluminosilicate mineral with the formula $Na_2O\text{-}Al_2O_3\text{-}2SiO_2$. When sulfates are captured within the cage structure, nosean forms with the formula $3Na_2O\text{-}3Al_2O_3\text{-}6SiO_2 \cdot Na_2SO_4$. When chlorides are captured within the cage structure, sodalite forms with the formula $3Na_2O\text{-}3Al_2O_3\text{-}6SiO_2 \cdot 2NaCl$. Depending on the waste compositions, process additives such as magnetite are included to form iron-bearing spinel minerals to sequester Cr and Ni in the waste.

The FBSR waste form is then the granular product encapsulated in a binder to minimize dispersability. A number of binders have been evaluated including ordinary Portland cement, high-alumina cements, geopolymers prepared with either kaolin clay or fly ash, various hydroceramic cements and an advanced silicone geopolymer composite material. A geopolymer binder prepared with fly ash has received the most extensive testing but a final binder has not been selected and further development and testing is underway.

The FBSR process has been demonstrated using nonradioactive simulants for Hanford LAW wastes and Idaho SBW. The FBSR process has not been demonstrated with the baseline Hanford caustic-scrubber secondary-waste stream from the WTP. The FBSR process has been demonstrated with a secondary-waste stream (WTP-SW) from the WTP based on an early LAW scenario in which the LAW melter submerged bed scrubber and wet electrostatic precipitator condensates are sent from the WTP as a secondary liquid stream for treatment. A testing program is currently underway using a bench-scale steam reformer and actual tank wastes.

Characterization data are available on the FBSR granular product prepared with the LAW, WTP-SW, and SBW simulants. This includes some contaminant release studies to support risk assessments and LAW waste form down selections in the early 2000’s. Some characterization data is also available on the various binders being evaluated.

8.1 Compliance with Waste Acceptance Criteria

The FBSR granular product encapsulated in a binder to form a monolith waste form will meet waste acceptance criteria for IDF. The FBSR process produces a dry granular material. Any free liquids would be introduced through the encapsulation process, and that process can be controlled to minimize/eliminate free liquids. The FBSR waste form has been shown to pass the TCLP required to meet IDF dangerous waste limitations. As with any waste form, if the concentrations of the COCs are too high, the waste form will not pass TCLP. At the expected concentrations in the secondary wastes, the FBSR product will easily pass TCLP. The FBSR waste form monoliths pass the 500-psi compressive strength requirement. Candidate binders include cements, geopolymers, and Ceramicrete.

Using rhenium as a surrogate for technetium, the FBSR waste form in the GEO-7 geopolymer binder has been shown to meet the target diffusivity for technetium for secondary wastes.

8.2 Robustness to Waste Stream Variations

Most researchers believe that FBSR is a robust technology because it accommodates wide ranges of feeds as well as high sulfate and other anions that are stabilized in aluminosilicate mineral cage structures (Jantzen 2006a). This has been shown in pilot-scale demonstrations with highly alkaline (pH = 14) and acidic (pH = 1) wastes. The FBSR process produces solid mineral phases from aqueous waste solutions that may have high concentrations of NaOH or sodium salts (3 to 5.2 M). These liquids can be made into carbonates, silicates, or NAS minerals, which may be produced under these conditions (Jantzen 2006a).

The process is also good for high alkaline earth and high carbon-containing wastes as well (Jantzen 2006a). Organic compounds are pyrolyzed in the presence of C and absence of air; superheated steam used as the fluidizing media converts C from all sources; nitrates and nitrites are converted to N_2 by adding a solid C source such as charcoal or sugar (Jantzen 2006a).

8.3 Simplicity in Production

The FBSR waste forms appear to be relatively easily produced. The FBSR technology is a moderate-temperature process (625 to 750 °C). The temperature is relatively low enough not to vaporize radionuclides, but it is high enough to destroy organic compounds and allow denitration, evaporation, dehydration, and hydrothermal reactivity to occur (Jantzen 2006a). Geophases (solid phases that contain contaminants) are also formed during this process. The FBSR process has been demonstrated at the pilot scale with Hanford LAW simulants and with a WTP LAW melter off-gas scrubber simulant.

Encapsulation of the FBSR granular product has been demonstrated at the laboratory scale with a range of binders, including geopolymers, hydroceramics, Ceramicrete, and cements. A binder has not been selected and the encapsulation process has not been scaled up, though most of the binder processes should be very straightforward.

8.4 Stability of Mineral Phases Under Relevant Conditions

FBSR materials were found to be as durable as glass with geometric surface area normalization and more durable than glass with BET surface area normalization (Jantzen 2006a). The FBSR LAW granular product has been characterized with respect to the PCT, PUF, and SPFT waste form durability tests to support evaluation of the technology as a supplemental treatment for Hanford LAW. Further testing is currently underway through the DOE-EM-31 Technology Development and Deployment (TDD) Program task on Fluidized Bed Steam Reformer Low-Level Waste Form Qualification.[1] The goal of the work is to reduce the risk associated with implementing the FBSR technology as a supplemental treatment for Hanford LAW by addressing the technical uncertainties associated with demonstrating acceptable performance for the FBSR product in a near-surface disposal facility. The planned testing includes:

- Quantitative XRD
- Chemical durability of pure phases

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[1] *Fluidized Bed Steam Reformer Low-Level Waste Form Qualification Task Plan*. Rev 0.0, September 2010. WP-5.2.1-2010-001, US Department of Energy, Washington, D.C.

- Chemical durability of non-radioactive FBSR product
- Evaluate the effect of coal and residual coal on contaminant release
- Chemical durability of radioactive BSR product
- Thermo-chemical measurements
- Secondary alteration phase formation
- Re, Tc, and I speciation in BSR product
- Diffusion release from monolith
- Pressurized unsaturated flow experiments.

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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 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	NA
		Volume returned to double-shell tanks (DSTs)(impacting stored waste volume)	NA

(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 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 (RPP-8402) were drafted. 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.	<u>4.3.1 Package Construction</u> 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.2. (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
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

Table B.2. (contd)

Property	Requirement	Basis	IDF Waste Acceptance Criteria[(a)]	Data Package Content
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[1], Rev 10, Section 3.36, Gas Generation. Some level of radiolytic decomposition may occur in the SSW and hydrogen may evolve.	<u>4.1.11 Gas Generation</u> 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	<u>4.3.5 Marking and Labeling</u> 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
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 WAC 173-303-665[2] (12); i.e., the container shall be at least ninety (90) percent full when placed in the landfill.	<u>4.1.4 Solidification and Stabilization</u> 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

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[1] - Hanford Site Solid Waste Acceptance Criteria. HNF-EP-0063.

[2] WAC – Washington Administrative Code. “Dangerous Waste Regulations.” WAC 173-303.

Table B.2. (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.	1.5 Waste Types Accepted for Disposal 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. 4.2.1 Radiological Concentration 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. 4.2.2 Dose-Equivalent Curie Limits 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. 4.2.3 Fissile Material Content 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.2. (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.2. (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	<u>4.1.13 Heat Generation</u> 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 71.1 ºC allowable design temperature at the primary geomembrane.	Radiogenic heat is not an issue. Document heat of curing. Curing time, set time.

Table B.2. (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	4.1.3 Liquids and Liquid Containing Wastes 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.2. (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.2. (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.2. (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
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.

Table B.2. (contd)

Property	Requirement	Basis	IDF Waste Acceptance Criteria[a]	Data Package Content
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.2. (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.	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).	ANSI/ANS 16.1 data. Include DI water data and data on other leachants.
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.2. (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: <u>Thermal Degradation</u>: 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. <u>Radiation Degradation</u>: 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.	<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).	Compressive strength data including radiation effects, water immersion, thermal cycling, biodegradation

Table B.2. (contd)

Property	Requirement	Basis	IDF Waste Acceptance Criteria[(a)]	Data Package Content
1.2.2.22 (contd)	Biodegradation: No evidence of culture growth when representative samples are tested in accordance with ASTM G21-96 and ASTM G22-76 (R1996), or equivalent methods Immersion degradation: 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	4.3.4 Handling 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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