U.S. DEPARTMENT OF
ENERGY

PNNL-20681

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

Secondary Waste Form Down Selection Data Package – Ceramicrete

KJ Cantrell
JH Westsik, Jr.

August 2011

Pacific Northwest
NATIONAL LABORATORY
Proudly Operated by Battelle Since 1965

PACIFIC NORTHWEST NATIONAL LABORATORY
operated by
BATTELLE
for the
UNITED STATES DEPARTMENT OF ENERGY
under Contract DE-AC05-76RL01830

Printed in the United States of America

Available to DOE and DOE contractors from the
Office of Scientific and Technical Information,
P.O. Box 62, Oak Ridge, TN 37831-0062;
ph: (865) 576-8401
fax: (865) 576-5728
email: reports@adonis.osti.gov

Available to the public from the National Technical Information Service,
U.S. Department of Commerce, 5285 Port Royal Rd., Springfield, VA 22161
ph: (800) 553-6847
fax: (703) 605-6900
email: orders@ntis.fedworld.gov
online ordering: http://www.ntis.gov/ordering.htm

PNNL-20681

Secondary Waste Form Down Selection Data Package – Ceramicrete

KJ Cantrell
JH Westsik, Jr.

August 2011

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

Pacific Northwest National Laboratory
Richland, Washington 99352

Summary

As part of high-level waste pretreatment and immobilized low activity waste processing, liquid secondary wastes will be generated that will be transferred to the Effluent Treatment Facility on the Hanford Site for further treatment. These liquid secondary wastes will be converted to stable solid waste forms that will be disposed in the Integrated Disposal Facility. Currently, four waste forms are being considered for stabilization and solidification of the liquid secondary wastes. These waste forms are Cast Stone, Ceramicrete, DuraLith, and Fluidized Bed Steam Reformer. The preferred alternative will be down selected from these four waste forms. Pacific Northwest National Laboratory is developing data packages to support the down selection process. The objective of the data packages is to identify, evaluate, and summarize the existing information on the four waste forms being considered for stabilization and solidification of the liquid secondary wastes. The information included will be based on information available in the open literature and from data obtained from testing currently underway. This data package is for the Ceramicrete waste form.

Ceramicrete is a relatively new engineering material developed at Argonne National Laboratory to treat radioactive and hazardous waste streams (e.g., Wagh 2004; Wagh et al. 1999a, 2003; Singh et al. 2000). This cement-like waste form can be used to treat solids, liquids, and sludges by chemical immobilization, microencapsulation, and/or macroencapsulation. The Ceramicrete technology is based on chemical reaction between phosphate anions and metal cations to form a strong, dense, durable, low porosity matrix that immobilizes hazardous and radioactive contaminants as insoluble phosphates and microencapsulates insoluble radioactive components and other constituents that do not form phosphates. Ceramicrete is a type of phosphate-bonded ceramic, which are also known as chemically bonded phosphate ceramics. The Ceramicrete binder is formed through an acid-base reaction between calcined magnesium oxide (MgO; a base) and potassium hydrogen phosphate (KH_2PO_4; an acid) in aqueous solution. The reaction product sets at room temperature to form a highly crystalline material. During the reaction, the hazardous and radioactive contaminants also react with KH_2PO_4 to form highly insoluble phosphates.

In this data package, physical property and waste acceptance data for Ceramicrete waste forms fabricated with wastes having compositions that were similar to those expected for secondary waste effluents, as well as secondary waste effluent simulants from the Hanford Tank Waste Treatment and Immobilization Plant were reviewed. With the exception of one secondary waste form formulation (25FA+25 W+1B.A. fabricated with the mixed simulant did not meet the compressive strength requirement), all the Ceramicrete waste forms that were reviewed met or exceeded Integrated Disposal Facility waste acceptance criteria.

Acknowledgments

The authors acknowledge technical reviews Ken Czerwinski (University of Nevada), Jim Krumhansl (Sandia National Laboratory), John Wiley (retired) and Shas Mattigod (Pacific Northwest National Laboratory) and word processing assistance by Kathy Neiderhiser and editorial review by Hope Matthews. Pacific Northwest National Laboratory is operated by Battelle Memorial Institute for the U.S. Department of Energy under Contract DE-AC05-76RL01830.

Acronyms and Abbreviations

ANL	Argonne National Laboratory
ANS	American Nuclear Society
ANSI	American National Standards Institute
ASTM	American Society for Testing and Materials
CBPC	chemically bonded phosphate ceramic
CFR	*Code of Federal Regulations*
CTF	Ceramicrete Treatment Facility
DOE	U.S. Department of Energy
DTA	differential thermal analysis
Ecology	Washington State Department of Ecology
ETF	Effluent Treatment Facility
FBSR	Fluidized Bed Steam Reformer
HLW	high-level waste
HSW	Hanford Waste Treatment and Immobilization Plant secondary waste
IDF	Integrated Disposal Facility
IHLW	immobilized high-level waste
ILAW	immobilized low activity waste
INTEC	Idaho Nuclear Technology and Engineering Center
LAW	low-activity waste
LDR	Land Disposal Restriction
MKP	magnesium potassium phosphate
NIST	National Institute of Standards and Technology
ORP	U.S. Department of Energy, Office of River Protection
PA	performance assessment
PCT	product consistency tests
PNNL	Pacific Northwest National Laboratory
PZC	point of zero charge
RCRA	*Resource Conservation and Recovery Act of 1976*
SEM	scanning electron microscopy
SBS	submerged-bed scrubbers
SBW	sodium-bearing waste
SNM	Special Nuclear Material
TCLP	Toxicity Characteristic Leaching Procedure
TRU	transuranic
UTS	Universal Treatment Standard
XRD	x-ray diffraction

WAC	*Washington Administrative Code*
WESP	wet-electrostatic precipitators
WRPS	Washington River Protection *Solutions*, LLC
WTP	Hanford Tank Waste Treatment and Immobilization Plant

Units of Measure

ºC	temperature in degrees Celsius
Mgal	megagallon (10^6 gallons)
MPa	megapascals
mrem	millirem
mSv	millisievert
psi	pounds per square inch

Contents

Figures

Tables

1.0 Introduction

The Hanford Site, located in southeastern Washington State, has 56 million gal of radioactive and chemically hazardous wastes stored in 177 underground tanks (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 is poured directly into stainless-steel canisters. The immobilized HLW (IHLW) canisters will ultimately be disposed of at an offsite federal repository. The immobilized LAW (ILAW) canisters will be disposed of onsite in the Integrated Disposal Facility (IDF). As part of the pretreatment and ILAW processing, liquid secondary wastes will be generated that will be transferred to the Effluent Treatment Facility (ETF) on the Hanford Site for further treatment. These liquid secondary wastes will be converted to stable solid waste forms that will be disposed in the IDF. Liquid effluents from the ETF will be discharged through the State Approved Land Disposal Site.

The ETF is an existing operating facility on the Hanford Site. It is a *Resource Conservation and Recovery Act of 1976* (RCRA) permitted multiwaste 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 after it comes on line for operations.

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

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

Washington River Protection *Solutions*, LLC (WRPS), a prime DOE contractor, is responsible for the ETF upgrades needed to receive secondary liquid wastes from the WTP. 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 treatment of 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 solidification of treated wastes from the ETF.

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

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

1.1 Origin and Disposition of Liquid Secondary Wastes from Hanford Tank Waste Treatment and Immobilization Plant

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

Both the HLW vitrification facility 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 (SBS) and wet-electrostatic precipitators (WESP). 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.

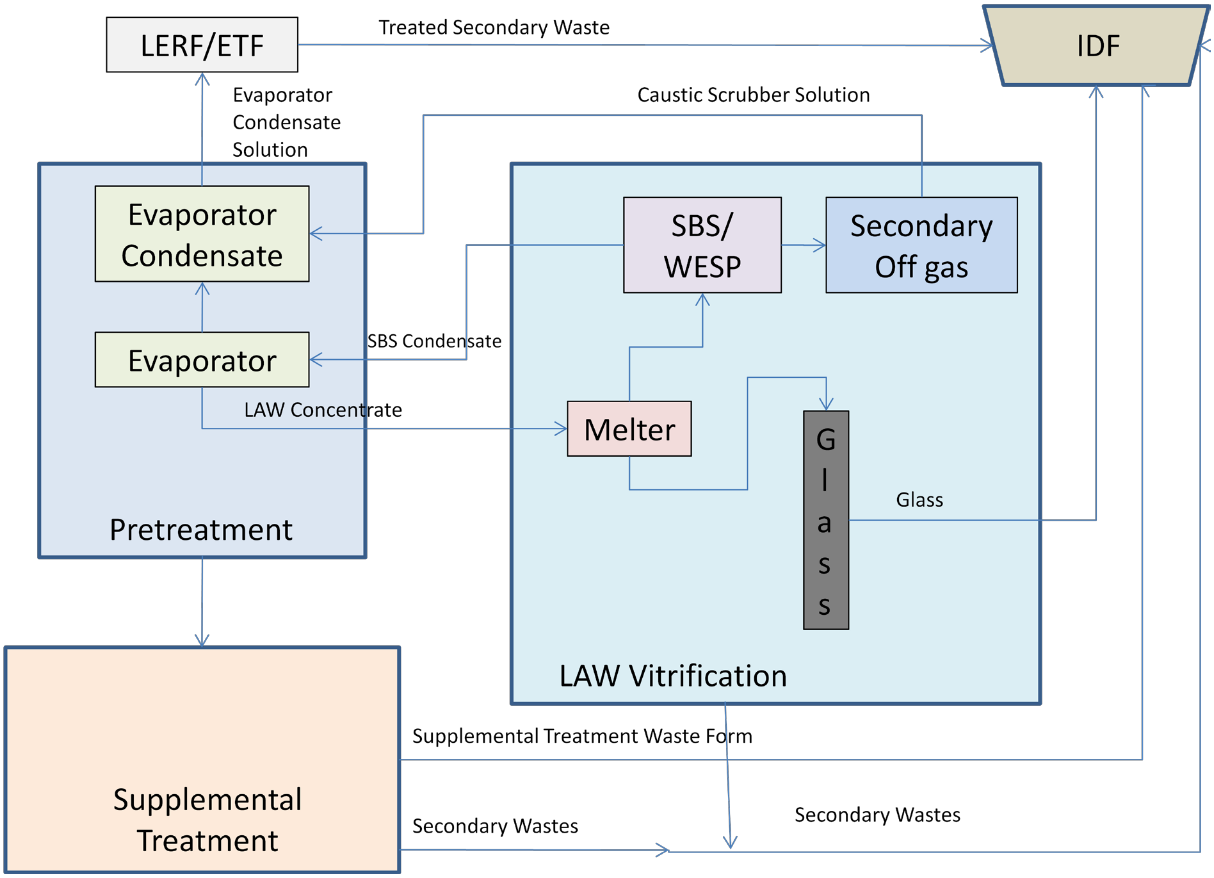


Figure 1.1. Schematic of Secondary Waste Sources

The LAW melter off-gas SBS and WESP condensate are recycled back to the pretreatment facility and ultimately back to the LAW melter. Under some operation scenarios, some or all of the condensate from the LAW melter off-gas SBS and WESP would go directly to a secondary waste stream exiting the WTP. For example, in an “early LAW” scenario, the LAW melter would begin operations using selected tank wastes before the pretreatment facility came on line. In this case, the SBS and WESP condensates would be combined with the caustic scrubber as a single liquid secondary waste stream from the WTP. In another scenario, a fraction of the SBS and 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 and 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, 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 the stabilization and solidification of radioactive and hazardous wastes. Radioactive high-level wastes from nuclear fuel reprocessing are converted to a glass waste form in stainless-steel canisters for disposal at a federal repository. Liquid low-level wastes and mixed radioactive and hazardous waste 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 solidification of WTP liquid secondary wastes. In 2006, PNNL completed an evaluation of three low-temperature waste forms including an alkali-alumino-silicate hydroceramic cement, DuraLith alkali alumino-silicate 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 alumino-silicate geopolymer and Ceramicrete phosphate-bonded ceramic as adequate waste forms for the secondary wastes. As part of the Advanced Remediation Technologies program, THOR Treatment Technologies and Savannah River National Laboratory (SRNL) demonstrated the feasibility of a 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 (THOR 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 form, several less mature technologies including several aluminosilicates and an iron-oxide mineral called goethite with the capacity to specifically retain technetium were identified. In parallel, WRPS issued a call for expressions of interest for secondary waste immobilization technologies. Responses to that call included a glass waste form produced with the Geomelt Vitrification Technology, a waste form based on the synroc ceramic titanate mineral, and a Nochar waste form prepared from a blend of acrylics and acrylamide copolymers (Pierce et al. 2010a).

Based on the technical literature and previous testing, four waste forms were selected for further testing and evaluation for the stabilization and solidification of WTP liquid secondary wastes. Included are the following:

- Cast Stone Portland-cement based waste form
- Ceramicrete phosphate bonded ceramic

- DuraLith alkali alumino-silicate 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 a FBSR waste form. At the conclusion of this current development and optimization task, PNNL plans on testing each optimized waste form to demonstrate compliance with the IDF criteria to support the final waste form selection. Part of that testing includes engineering-scale demonstrations of the DuraLith and Ceramicrete waste form processes and characterization of the resulting engineering-scale waste form products.

1.3 Secondary Waste Form Down Selection Data Package Content

In defining the content to be provided in the waste form down selection data packages, previous waste form selection processes at the Hanford Site were examined. In 2002, DOE implemented a plan to accelerate 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, and 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 supplemental waste form selection (shown in Table 1.1).

In addition, 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 and uncertainties and the testing objectives that should be addressed to resolve the identified issues and uncertainties for the containerize grout technology.

Types of data were identified to address each of the goals, criterion, and measures developed for the supplemental treatment down selection, and the technical issues/uncertainties and testing objectives recommended for the containerized grout. Appendix A includes expanded Tables 1.1 and 1.2 with the data package contents to address each measure and testing objective.

1.4 Integrated Disposal Facility 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; however, it does require the following:

> 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.

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

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

(a) Raymond et al. (2004).

IDF waste acceptance criteria have not been established for wastes to be disposed in the facility. There have been several draft WAC 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 WAC (RPP 2005) and the data package content to address each criterion. Included are criteria with respect to free liquids, compliance with LDRs, compressive strength, and leachability. For the purposes of the secondary waste form down selection, the following requirements apply:

- LDRs: The waste form will meet the land disposal requirements in 40 *Code of Federal Regulations* (CFR) 268 by meeting the universal treatments standards in 40 CFR 268.48 via the Toxicity Characteristic Leaching Procedure (TCLP) test.

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

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

(a) Josephson et al. (2003).
LDR = Land disposal restriction.
PA = Performance assessment.

- Free Liquids: The waste form shall contain no detectable free liquids as defined in SW-846 Method 9095
- Leachability Index: The waste form shall have a sodium leachability index greater than 6.0 when tested in deionized water using the ANSI/ANS-16.1 method (ANS 1986) or EPA Method 1315. The waste shall have a rhenium or technetium leachability index greater than 9.0. These requirements are based on the Nuclear Regulatory Commission's *Technical Position on Waste Form* (NRC 1991), early waste disposal risk assessments, and performance assessment 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 3.54E6 Pa (500 psi) when tested in accordance with ASTM C39/C39M. This requirement is based on *Technical Position on Waste Form* (NRC 1991), which is more restrictive for cement-based waste forms.

1.5 Data Package Content

The data package begins with a description of the waste form in Section 2.0. This includes the primary waste form, any encapsulating materials, waste form packaging, and types of wastes tested. Section 3.0 describes the waste form preparation process including starting materials and processing steps. Section 4.0 expands upon the information in Section 3.0 to include flow sheet 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 5.0. Section 6.0 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 7.0. Section 8.0 concludes with a summary of the strengths and weaknesses of the waste form.

2.0 Waste Form Description

The Ceramicrete disposal package will include the Ceramicrete waste form itself and a container for protection of the waste form during handling, transportation and storage.

2.1 Ceramicrete Description

Ceramicrete is a relatively new engineering material developed at Argonne National Laboratory (ANL) to treat radioactive and hazardous waste streams (e.g., Wagh 2004; Wagh et al. 1999a, 2003; Singh et al. 2000). This cement-like waste form can be used to treat solids, liquids, and sludges by chemical immobilization, microencapsulation, and/or macroencapsulation. The Ceramicrete technology is based on chemical reaction between phosphate anions and metal cations to form a strong, dense, durable, and low porosity matrix that immobilizes hazardous and radioactive contaminants as insoluble phosphates and microencapsulates insoluble radioactive components and radioactive components that do not form phosphates. Ceramicrete is a type of phosphate-bonded ceramic, which are also known as chemically bonded phosphate ceramics (CBPC). The Ceramicrete binder is formed through an acid-base reaction between calcined magnesium oxide (MgO; a base) and potassium hydrogen phosphate (KH_2PO_4; an acid) in aqueous solution:

$$MgO + KH_2PO_4 + 5H_2O \rightarrow MgKPO_4{\cdot}6H_2O \tag{2.1}$$

The resulting magnesium potassium phosphate (MKP) phase is used as a matrix material to form a concrete-like waste form that is very stable, with a solubility product of 2.4×10^{-11} under ambient conditions (Taylor et al. 1963). The reaction product sets at room temperature to form a highly crystalline material. During the reaction, the hazardous and radioactive contaminants also react with KH_2PO_4 to form highly insoluble phosphates. The bulk ceramic then microencapsulates the reacted contaminants in the dense crystalline MKP matrix. X-ray diffraction (XRD) of the ceramic indicates the presence of only the MKP phase and unreacted MgO (Wagh 2004). Similarly, scanning electron microscopy (SEM) indicates the presence of only MKP crystals. Information regarding the MKP phase is sparse. Both Sivaprasad et al. (1990) and Wagh et al. (1999b) have determined its crystal structure and considered this material to be an analog of struvite ($NH_4MgPO_4{\cdot}6H_2O$), in which NH_4 is replaced by K. Differential thermal analysis (DTA) and thermogravimetric analysis indicate that the 6 mol of water in the crystal are loosely bound and are released upon heating at 120ºC, after which anhydrous MKP is formed.

Ceramicrete meets waste disposal acceptance criteria, including compressive strength and universal treatment standards for RCRA metals (as measured by the TCLP [EPA 1992]) to be acceptable for land disposal. The performance and physical properties of the Ceramicrete waste form can be enhanced through addition of silica in the form of fly ash or wollastonite ($CaSiO_3$) (Wagh 2004; Wagh et al. 1999a). Compressive strengths of enhanced Ceramicrete are high, typically ranging from 55 to 83 MPa (8000–12,000 psi) (Wagh 2004). In addition to the high strength of the Ceramicrete composites, the ability to form large castings in nearly any desirable configuration (e.g., 55-gal barrels or 4-ft × 4-ft × 4-ft cubes) is a major advantage.

Ceramicrete has been tested and used to stabilize a variety of waste categories including hazardous wastes, radioactive wastes, and mixed wastes. Additionally, Ceramicrete has been tested and used to stabilize a wide range of solid and aqueous waste streams, including ash, soils, sludges, and debris (Singh et al. 1997, 1998; Wagh 2004; Wagh et al. 1997, 1999b). In some cases, reductants have been used to reduce the leachability of certain components such as Ag, Cr(VI), and Tc(VII) from the waste form (Singh et al. 2006; Wagh 2004; Wagh et al. 2003). Reductants that have been used include Na_2S, K_2S, and $SnCl_2$. Addition of silver zeolite has been used to enhance iodine precipitation (Russell et al. 2006).

Because the scope of this data package is to support evaluation and selection of waste forms for stabilization and solidification of the liquid secondary waste stream from the WTP, detailed discussions of Ceramicrete performance will focus primarily on liquid waste streams that have similar compositions—in some respects—to the secondary waste stream composition expected from the WTP. The secondary waste stream will be composed of liquid wastes from the caustic scrubber in the LAW vitrification facility and evaporator condensates from the pretreatment plant. The caustic scrubber is downstream of the primary LAW vitrification off-gas treatment system and is expected to capture volatile iodine, RCRA metals, and technetium not removed earlier in the process. The primary contaminants of concern in the secondary waste stream are expected to be ^{99}Tc, ^{129}I, Ag, Cd, Cr, Hg, and Pb (Pierce et al. 2010b). Major components of the secondary waste are expected to consist of sodium (2 M), aluminum (0.2 M), hydroxide (1.2 M), nitrate (0.69 M), and oxalate (0.23 M) (Pierce et al. 2010b).

2.1.1 Ceramicrete Formulations for Secondary Wastes

Ingredients for Ceramicrete waste forms include magnesium oxide, mono potassium phosphate, and water. Filler materials such as calcium silicate or wollastonite, fly ash, blast furnace slag are added to reduce costs and may actually improve the performance of the Ceramicrete. To reduce the mobility of some contaminants, getter materials are added. Silver zeolite is typically used to retain iodine. Tin chloride is added to reduce technetium and rhenium, which is frequently used as a surrogate for technetium, from the +7 oxidation state to the less mobile +4 oxidation state. Blast furnace slag also helps with this reduction. Sodium sulfide may be added to form the more insoluble sulfide forms of mercury (HgS) and chromium (CrS) (Russell et al. 2006).

Table 2.1 shows the Ceramicrete formulations used in the first Ceramicrete secondary waste forms and for the Idaho Sodium Bearing Waste (SBW) (Russell et al. 2006). These formulations were not optimized but provided an initial laboratory-scale demonstration of the Ceramicrete to these waste streams.

After further testing with different secondary waste simulant solutions and a range of mixes of filler materials, a more refined Ceramicrete formulation was recommended for further characterization with respect to waste form leachability and for engineering-scale demonstrations with the Ceramicrete and simulated secondary waste streams (Singh et al. 2011). This composition is also shown in Table 2.1.

2.1.2 Chemical Compositions of Ceramicrete Waste Forms

Table 2.2 lists the chemical composition of Ceramicrete waste forms prepared with Hanford secondary waste simulants and Idaho SBW simulants.

X-ray absorption near edge spectroscopy examination of a Ceramicrete specimen prepared with a technetium-99-spiked caustic scrubber simulant (see Table 2.5 below) and cured for 3 days showed that the technetium present was nearly 100 percent reduced to the Tc(IV) oxidation state (Um et al. 2011).[1]

Table 2.1. Ceramicrete Waste Form Components in Weight Percent

Ingredient	Idaho Sodium Bearing Waste (from Russell et al. 2006)	Hanford Secondary Waste (from Russell et al. 2006)	Hanford Secondary Waste (from Singh et al. 2011)
MgO	9.3	12.0	9.5
KH_2PO_4	27.8	35.9	32.4
$CaSiO_3$	11.4	14.4	-
Fly Ash (Class C)	-	-	34.3
Silver Zeolite	1.06	1.2	1.1
$SnCl_2$	0.42	0.47	1.3
Na_2S	0.42	-	-
Waste Simulant	47.4	25.8	19.6
Water	-	-	1.8
NaOH (neutralizer)	2.2	-	-
H_3PO_4 (neutralizer)	-	10.1	-

Table 2.2. Ceramicrete Waste Form Compositions in Weight Percent

Constituent	HSW	SBW
Ag	0.0018	2.74E-06
Al	0.009	1.19
B	2.62E-05	0.0075
Ca	5.06	4.08
Cd	2.89E-05	0.0047
Ce	1.50E-07	4.98E-05
Cl	0.178	0.230
CO_3^{2-}	4.40	--
Cr	4.56E-05	0.0105
Cs	1.25E-06	1.49E-06
F	--	0.0529
Fe	4.61E-05	0.0641
Hg	6.45E-06	0.0188
I	2.70E-05	2.18E-04
K	10.5	8.49
Mg	6.89	5.63

---

[1] Um, W, RJ Serne, MM Valenta, KE Parker, C-W Chung, G Wang, JS Yang, KJ Cantrell, MH Engelhard, and JH Westsik, Jr. 2011. *Radionuclide Retention Mechanisms in Secondary Waste Form Testing: Phase II*. Draft, Pacific Northwest National Laboratory, Richland, Washington.

Table 2.2. (contd)

Mn	--	0.0415
Na	3.57	4.74
NO_3^-	0.114	17.1
Pb	0.0017	0.0171
P	11.6	6.37
Re	9.14E-06	4.05E-05
S	--	0.282
Si	3.55	2.77
Sn	0.299	0.263
TOC	1.02	--
H_2O	14.9	22.0
Total	62.14	73.38

2.2 Waste Form Package

The waste form container/package provides both protection and containment for the waste form during production, transportation, and storage. A waste form container or package has not been selected for the waste form (Cast Stone, DuraLith, Ceramicrete, or FBSR). The waste form container will need to meet requirements for transporting radioactive and hazardous materials as specified in 49 CFR 173. The materials of construction for the package must be compatible with the wastes and with the protective liners included in the IDF design. Generally, the package will be fabricated of the following materials, which are 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 container size will be dictated by critically safety considerations. A critically safety evaluation for the IDF qualified the following container sizes:

- Fifty-five gal (208 L, 0.21 m^3) drums, 57.15 cm diameter × 88.14 cm high (22.5 in. diameter × 34.7 in. high)
- Eighty-five gal (322 L, 0.32 m^3) drums, 66 cm diameter × 100.3 cm high (26 in. diameter × 39.5 in. 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.

Container size will also be constrained by waste form processing and curing considerations. Any elevated temperatures of the waste form slurry as it is poured into the container will need to be dissipated, as will any heat generated by the curing processes for the waste form. The container will need to be sized and filled such that the heat dissipates without impacting the quality of the waste form. The Ceramicrete reaction between the MgO and KH_2PO_4 is exothermic with temperatures as high as 82ºC reported for large scale construction application of Ceramicrete in bridges and storage silos for nuclear materials (Russell et al. 2006).

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

2.3 Range of Wastes and Compositions Tested for Ceramicrete

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

2.3.1 Composition of Wastes

The Ceramicrete formulations have been optimized for a range of liquid wastes, including HSWs and Idaho SBWs. The compositions of HSWs and SBWs that were tested during the years 2005 to 2006 are listed in Tables 2.3 and 2.4. The HSW simulant was mainly an ~2 M sodium carbonate solution with minor concentrations of nitrate, hydroxyl, and total organic carbon (TOC) and trace concentrations of Ag, Cr, Cd, I Re(Tc), Hg, and Pb. The Idaho SBW was an acidic ~1.9 M sodium nitrate solution with other minor and trace constituents (Table 2.4).

Table 2.3. Composition of WTP HSW Waste Used for Ceramicrete Formulation

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

Table 2.3. (contd)

TOC	0.18	13.86	13.86

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

In more recent Ceramicrete waste form development and optimization, three simulant compositions were used to represent the variability in the composition of the caustic scrubber secondary waste stream. The caustic scrubber is downstream of the primary LAW vitrification off-gas treatment system and is expected to capture volatile iodine and technetium not removed earlier in the process. Further, as part of the overall secondary off-gas treatment system, the caustic scrubber is downstream of the high-efficiency particulate air (HEPA) filters used for particulate removal, the carbon beds for mercury removal, and the selective catalytic reduction beds for oxidizing volatile organic compounds SO_x and carbon monoxide and for NO_x reduction. The caustic scrubber liquid effluents are returned to the pretreatment plant where they are combined with the pretreatment evaporator condensates and sent to the LERF/ETF, becoming the source of the secondary wastes requiring treatment. In addition, this report used another (a fourth) simulant to represent the blended caustic scrubber/submerged bed scrubber (SBS)/wet electrostatic precipitator (WESP) liquid waste stream.

Table 2.4. Composition of Idaho SBW Waste Used for Ceramicrete Formulation

Element	Target (moles/L)	Target (g/L)	Analysis (g/L)	Element	Target (moles/L)	Target (g/L)	Analysis (g/L)
Na	1.88	43.24	43.2	Ce	5.30E-06	7.43E-04	7.82E-04
Al	0.575	15.5	17.8	Hg	0.002	0.401	0.4
Ca	0.0366	1.464	1.46	Pb	0.0013	0.269	0.27
B	0.0102	0.11	0.11	Re (Tc)	3.13E-06	5.83E-04	6.37E-04
Mg	0.0108	0.26	0.26	I	5.66E-05	7.18E-03	3.43E-03
K	0.175	6.825	6.8	SO_4^{2-}	0.0491	4.71	5.15
Cr	0.0033	0.172	0.172	H_2O	45.1	812.7	812
Mn	0.0126	0.69	0.69	NO_3^-	4.91	304.4	269
Fe	0.0178	0.993	0.99	F^-	0.0403	0.765	0.83
Cd	0.0007	0.0786	0.078	Cl^-	0.0285	1.009	1.15
Cs	7.99E-10	1.10E-07	2.34E-05	H	1.87	1.87	NA

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

The target compositions shown in Table 2.5 are adapted from an analysis of a G2 flow sheet model run (MRQ 09-0019 Scenario 5.0.22a). The compositions are based on the spreadsheet "Secondary Waste

Expected Liquid Waste Composition, rev 1.xlsx" provided to PNNL by WRPS.[1] This spreadsheet provides estimates of the caustic scrubber composition for 241 monthly times. The projected compositions include 32 components (not counting Na and ones that only had zero values), but only 11 of them plus sodium represent more than 99.9 percent of the non-aqueous molar content of the waste. These 11 components are OH^-, NO_3^-, Al, CO_3^{-2}, Cl^-, NO_2^-, PO_4^{-3}, SO_4^{-2}, Si, K, and F^-. Other components, such as RCRA metals and ^{99}Tc, are relevant to waste form performance and were included in the simulants. Before selecting the simulant compositions, the compositions for each of the 241 monthly times was charge balanced for the 11 components using sodium and then normalized to a constant sodium concentration (moles per mole Na).

The S1 simulant composition is the median composition (Table 2.5). It was developed by taking the monthly composition estimates from the G2 model over the 241 dates provided and determining the median value for each species over the data set provided. This yielded the concentrations for OH^-, NO_3^-, CO_3^{-2}, Cl^-, F^-, NO_2^-, PO_4^{-3}, SO_4^{-2}, Si, K, Al, and NH_4^+.

Table 2.5. Composition of WTP Secondary Waste Simulants Proposed for Phase 2 Testing

Element (mole/liter)	S1(a) Caustic Scrubber Median	S2(a) Statistical – Cluster 1 3/16/2038	S3(a) Statistical – Cluster 2 05/28/2024	S4(a) Caustic Scrubber /10% of SBS Blend	Phase 1 Simulant	Target Russell et al. (2006)
Na	1	1	1	1	2.0	2.0
$Al(OH)_3$	9.39E-02	1.14E-01	9.22E-02	4.24E-02	0.23	0.011
Si	1.88E-03	2.04E-03	7.74E-04	1.39E-02	-	-
K	5.82E-04	6.51E-04	2.18E-03	2.87E-02	-	-
NH_4^+ (total)	---	---	---	4.41E-01	-	-
OH^-	3.98E-01	3.98E-01	3.98E-01	1.02E-08	1.2	0.094
NO_3^-	3.28E-01	1.90E-01	3.97E-01	1.13E+00	0.69	0.018
CO_3^{-2}	2.28E-02	4.66E-02	3.94E-02	1.04E-02	1.5E-6	0.96
Cl^-	2.25E-02	2.17E-02	2.91E-02	1.04E-02	-	-
NO_2^-	1.20E-02	1.05E-02	3.83E-02	4.31E-02	-	-
PO_4^{-3}	6.87E-03	4.85E-03	6.03E-03	5.10E-03	1.7E-2	-
SO_4^{-2}	4.41E-03	5.81E-03	5.14E-03	4.36E-02	9.7E-3	-
F^-	5.57E-04	3.75E-04	4.42E-04	1.02E-08	-	-
Cr	2.03E-04	2.03E-04	2.03E-04	1.09E-03	8.43E-3	2.8E-04 (100x)
Ag	6.27E-06	6.27E-06	6.27E-06	2.35E-05	2.5E-4 (100x)	2.2E-04 (100x)
As	3.48E-05	3.48E-05	3.48E-05	1.61E-05	-	-
Cd	1.57E-06	1.57E-06	1.57E-06	2.16E-05	5.0E-5 (100x)	1.4E-05 (100x)
Hg	1.13E-05	1.13E-05	1.13E-05	5.30E-06	3.3E-5 (1x)	2.4E-06

---

[1] Josephson GB, GF Piepel, and JH Westsik, Jr. 2010. *Selection of Secondary Waste Test Compositions*. Pacific Northwest National Laboratory, Richland, Washington.

Table 2.5. (contd)

Pb	8.99E-06	8.99E-06	8.99E-06	8.28E-06	7.9E-4 (100x)	1.5E-04 (100x)
Tc	1.81E-05	1.81E-05	1.81E-05	5.59E-04	7.7E-06	-
^{99}Tc (Ci/Liter)	3.05E-05	3.05E-05	3.05E-05	9.41E-04	1.3E-5 Ci/L	
Re	1.81E-05	1.81E-05	1.81E-05	5.59E-04	-	6.00E-07 (Re)
I^-	4.62E-06	4.62E-06	4.62E-06	6.29E-05	2.9E-6	2.90E-06
^{129}I (Ci/Liter)	9.53E-08	9.53E-08	9.53E-08	1.30E-06		
TOC (as oxalate)	9.39E-02	1.14E-01	9.22E-02	4.24E-02	0.23	0.18

(a) Simulant compositions shown at 1 M Na. Actual target compositions were in the range of 2 M to 10 M Na.

The RCRA metals, technetium, and iodine concentrations chosen were based on their maximum concentrations (moles per mole Na) over the 241 dates. In a few cases, it was still necessary to increase the concentrations of selected species to facilitate reasonable analytical detection limits in the testing.

The two "cluster" compositions are based on a statistical analysis of the same G2 model set after charge balancing and were normalized to a constant sodium concentration. In this case, seven dates and corresponding data points were removed as apparent outliers, and the analysis was conducted on the remaining 234 compositions. A cluster analysis of the data showed that the compositions appear to fall into one of two clusters. Two waste compositions were selected from the 234 "realistic" G2 model compositions, one from each cluster. The two representative clusters were selected to maximize the range in concentrations of nitrate plus chloride.

- Simulant S2 is from Cluster 1 and represents a low nitrate plus chloride concentration for that cluster. This is the 3/16/2038 projected composition in the G2 CS data set.
- Simulant S3 is from Cluster 2 and represents a high nitrate plus chloride concentration for that cluster. This is the 5/28/2024 projected composition in the G2 CS data set.

Because of the need to increase the analytical sensitivity for some of the RCRA metals (namely Ag, As, Cd, and Pb), the concentrations of these COCs were spiked at 10 to 100 times their maximum expected concentration. The concentration of Cr and Hg were not increased because the simulant concentration for these is sufficient to achieve the analytical sensitivity required to obtain quantitative information from these leach experiments. The same maximum RCRA metal concentrations were used for the three caustic scrubber simulants (S1, S2, and S3). One batch of simulant was prepared and used to make samples of the Cast Stone waste. The three caustic scrubber waste simulants were prepared by mixing 18 MΩ-cm DIW with reagent-grade chemicals.

The fourth simulant (S4) represents the caustic scrubber blended with a bleed stream from the SBS condensate tank, which will receive liquids from the low-activity waste melter SBS and WESP. For this simulant, it was assumed that 10% of the SBS recycle stream is purged to prevent a buildup of species such as chlorides or sulfates. As mentioned, Table 2.1 shows the four simulants used for the Cast Stone testing. The table also shows the simulant used in the Phase 1 testing (Pierce et al. 2010b) as well as an earlier secondary waste simulant used in an earlier low-temperature immobilization study (Russell et al.

2006). Components that cannot be detected within the detection limits will be reported as “below the limit.” The technetium concentrations used in each simulant were kept above 10^{-5} mole/liter regardless of the calculated target concentrations to facilitate detecting technetium in the leachates. All four simulants were analyzed using wet chemical analysis to verify how close they were to the target compositions.

2.3.2 Waste Loading and Sodium Molarity

The waste loadings achieved on a solid waste basis during the low temperature waste immobilization testing (Russel et al. 2006) and during secondary waste form testing of ceramicrete (Singh et al. 2011) are listed in Table 2.6. The HSW and SBW simulants were partially neutralized to a pH of 5 with H_3PO_4 and NaOH, respectively. The highest waste loading used in Singh et al. (2011) were significantly lower than those used in Russel et al. (2006) particlularly for the HSW S1 waste.

Table 2.6. Solid Waste Loadings in Ceramicrete Waste Forms

	HSW[(a)]	SBW[(a)]	HSW S1[(b)]	HSW S1[(b)]	HSW S4[(b)]	HSW S4[(b)]
Waste form properties			45FA+20W	45CaSi+20W	45FA+20W	45CaSi+20W
Waste Loading (wt. %)	2.87%	14.2%	1.31%	1.35%	2.31%	2.23%
Na Conc. (M)	2	1.9	1	1	1	1

(a) Russel et al. (2006); (b) Singh et al. (2011)

3.0 Ceramicrete Process Description

The Ceramicrete preparation process is relatively simple. Getter materials such a tin chloride and silver zeolite are added to the liquid waste solution. Then the magnesium oxide and mono potassium phosphate and any fillers are added. The slurry is mixed and is poured into the container to cure. This section includes a description of the ingredients, process steps and times, temperatures, and curing. After this a description of the Ceramicrete process chemistry is provided.

3.1 Ceramicrete Waste Form Ingredients

The primary ingredients of Ceramicrete are magnesium oxide, potassium mono phosphate, and water. The MgO and KH_2PO_4 are added in the percentages of 23 weight percent MgO and 77 weight percent KH_2PO_4. Table 3.1 lists the main ingredients and suggested sources.

Table 3.1. Ceramicrete Dry Materials and Potential Sources

Material	Suggested Sources
MgO (magnesium oxide)	
MgO P98	Martin Marietta Magnesia Specialties, MD
MKP (mono potassium phosphate)	
MKP-771	Bindan Corp., Oakbrook, IL ICL Performance Products, Saint Louis, MO
Powder Filler	
Class C Fly Ash	La Farge, Chicago, IL
Calcium silicate (Wollastonite)	NYCO, Willsboro, NY
Blast furnace slag	La Farge, Chicago, IL
Additives	
Boric acid, Technical grade, H_3BO_3	Fisher Scientific
Tin chloride, $SnCl_2$, 98% Reagent grade	Sigma Aldrich
Ag-loaded zeolite (Ionex Type Ag 400)	Molecular Products, Golden, CO
Potassium sulfide (I-5130)	Chem Service
Water	Local source

3.2 Ceramicrete Process Steps

The following steps were followed in the preparation of a 55-gallon drum of Ceramicrete using a simulated secondary waste solution.

3.2.1 Ingredient List

Table 3.2 lists the batch recipe used for a 51-gallon batch of Ceramicrete. Boric acid was added as a set retarder.

Table 3.2. Ingredients for a 51-Gallon Batch of Ceramicrete

Component	Chemical Formula	Weight %	Calculated Weights, Kg
1M Na^+ Simulant	--	19.60	75.68
Dry Components		78.84	304.40
Magnesium Oxide	MgO	9.53	36.80
Mono Potassium Phosphate	KH_2PO_4	32.41	125.14
Class C Fly Ash	--	34.31	132.47
Stannous Chloride	$SnCl_2 \cdot 2H_20$	1.50	5.79
Ground Zeolite – 5A	--	1.09	4.21
Supplemental Water	H_2O	1.56	6.02
Totals before boric acid		100	386.10
Boric acid		0.5	

3.2.2 Process

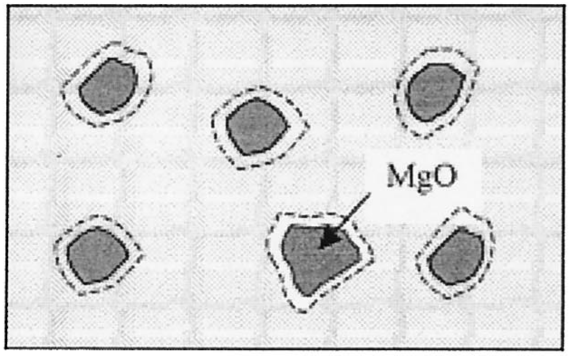
1. Weigh the prescribed MgO, KH_2PO_4, and fly ash solids into a mixer and thoroughly mix. Empty the solids from the mixer and save for re-addition, or mix the prescribed solids in another mixer.
2. To the empty mixer, add prescribed weight of 1M Na waste simulant and continue mixing.
3. Add prescribed weight of $SnCl_2$ and mix for an additional 4 min.
4. Add prescribed weight of zeolite 5A and mix for an additional 3 min.
5. Add prescribed weight of supplemental H_2O.
6. Add prescribed weights of previously mixed solids and continue to mix.
7. Mix 15-20 min. and pour slurry into waste container.

3.3 Ceramicrete Chemistry

Mg-phosphates are the most developed and studied of the CBPCs and have found several commercial applications including stabilization and solidification of low-level radioactive and hazardous waste (Wagh 2004). A general dissolution model of the kinetics of formation of CBPCs was developed by Wagh and Jeong (2003). A description of this model from Wagh and Jeong (2003) is summarized below.

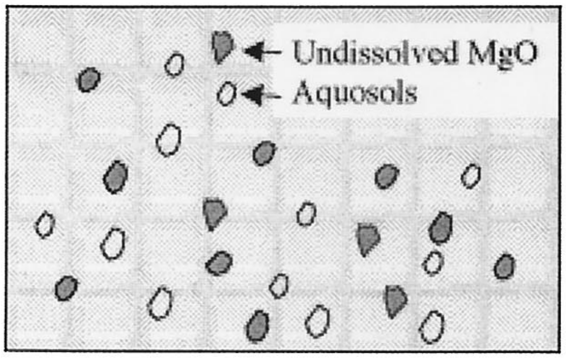
CBPCs are formed by slowly stirring oxides of metals into an acid phosphate solution such as H_3PO_4, $(NH_4)_2HPO_4$, $(NH_4)H_2PO_4$, $Al(H_2PO_4)_3$, or KH_2PO_4. Dissolution and dissociation of the acid leads to the formation of ions of phosphates and protons in solution, making the solution acidic. When oxides of metals are stirred into such an ion-rich solution, they go through a number of transformations. The kinetics of these transformations are very similar to the conventional sol-gel process of fabricating ceramics of nonsilicates (Brinker and Scherer 1989), with the major difference being the acid-base reaction used in forming CBPCs carries the mixture all the way to formation of ceramics. In the sol-gel process, the sols are ultimately sintered to form superior ceramics. The step-by-step reactions leading to formation of CBPCs is illustrated in Figure 3.1. When metal oxides are stirred into an acid solution, they

a. Dissolution of oxide



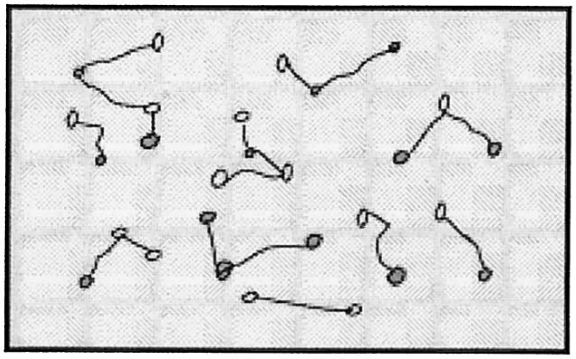
$MgO + H_2O \rightarrow Mg^{2+}(aq) + 2OH^-$

b. Formation of aquosols



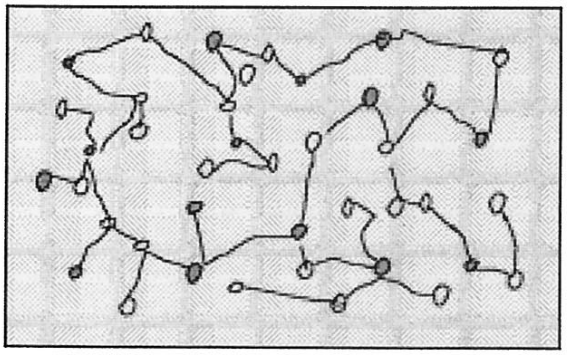
$Mg^{2+}(aq) + :O<^{H}_{H} \rightarrow [Mg \leftarrow O^{\rightarrow H}_{\rightarrow H}]^{2+}(aq)$

c. Acid-base reaction and condensation



$$Mg(OH)^{2+}(aq) + HPO_4^{2-} + 2H_2O \\ \rightarrow MgHPO_4.3H_2O$$

d. Percolation and gel formation



e. Saturation and crystallization

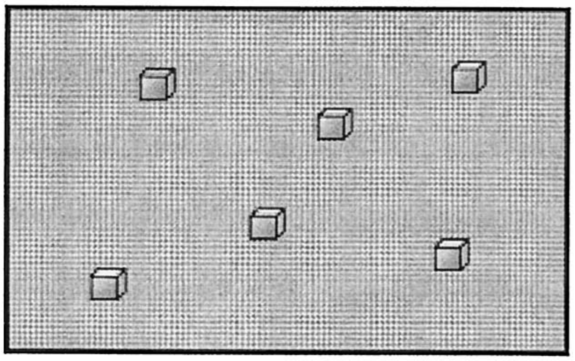


Figure 3.1. Diagrammatic Representation of Formation of Chemically Bonded Phosphate Ceramics (from Wagh and Jeong 2003)

dissolve slowly, releasing metal cations and hydroxide (Figure 3.1a, dissolution step). The cations react with water molecules and form positively charged "aquosols" through hydrolysis (Figure 3.1b, hydration step). The dissolution and hydrolysis are the rate-controlling steps in forming CBPCs. As illustrated in Figure 3.1c, the sols subsequently react with aqueous phosphate anions to form hydrophosphate salts, while protons react with hydroxide to form water. The newly formed hydrophosphate salts form a network of molecules in solution that leads to formation of a gel (Figure 3.1d). As the reaction proceeds, this process introduces more and more reaction products into the gel, and it thickens. When sufficiently thickened, the gel crystallizes around the unreacted core of each particle of the metal oxide into a well-connected crystal lattice that grows into a monolithic ceramic (Figure 3.1e).

The dissolution step determines which oxides will form a ceramic and which will not, while the hydration step determines the pH range in which the ceramics will form. The formation of a well-crystallized ceramic or a poorly crystallized precipitate will depend on how slowly or rapidly the dissolution of the oxides occurs in the acid solution. The overall acid-base reaction is exothermic, providing heat to the reaction slurry. If this heat raises the temperature of the slurry beyond its boiling point, the slurry will boil over and disrupt the formation of the ceramic. Therefore, the reaction rate of the dissolved species should be slow so the heating of the slurry is not excessive. Thus, the basic two requirements for forming a well-crystallized CBPC are the following: 1) the solubility of the oxides in the solution should be sufficiently high for the formation of a saturated gel but also sufficiently low to allow slow crystallization of the gel; 2) the rate of exothermic heat production and hence the dissolution rate of oxides should be sufficiently slow to allow the phosphate gel to crystallize slowly into a well-ordered crystal lattice without interruption, and grow into a monolithic ceramic. These two requirements put upper and lower limits on the solubility of the oxides that can be used to form CBPCs. If the solubility of the oxides is too high, a precipitate is formed, whereas if it is too low, the oxides will not react. These requirements may be quantitatively formulated through consideration of the thermodynamic properties of the oxides in the phosphate solution.

Consider first the dissociation of H_3PO_4 itself. The solubility of H_3PO_4 is high and its dissociation reaction in solution is given by Equation (3.1).

$$H_3PO_4 = mH^+ + H_{3-m}PO_4^{m-} \ (m = 0\text{–}3) \qquad (3.1)$$

The superscript represents the ionic charge. For pH < 2.1, there is little dissociation of the acid and H_3PO_4 is the dominant phosphate species in solution (m = 0). Between pH 2.1 and 7.2, $H_2PO_4^-$ is the dominant species (m = 2). Between pH 7.2 and 12.3, HPO_4^{2-} is the dominant species (m = 2). When an alkaline oxide—such as MgO—is stirred into an acid phosphate solution, the pH of the solution will slowly rise as acid is neutralized. As the pH rises above 2, formation of ceramics is initiated. The dissolution reaction of a metal oxide MO_n in an acidic solution is shown in Equation (3.2):

$$MO_n + 2nH^+ = M^{2n+}(aq) + nH_2O \qquad (3.2)$$

where M is a metal of a valency 2n, and (aq) indicates an aqueous ion. Dissolution of the metal oxide neutralizes protons, increasing the pH of the solution. This can lead to hydrolysis of some cations to produce species of the form $MOH_x^{(2n-x)}(aq)$. Examples for MgO and Al_2O_3 include $Mg(OH)^+$, $Al(OH)^{2+}$ and $Al(OH)_2^+$. For the dissolution reaction given by Equation (3.3), the equilibrium constant K is defined as

$$K_n = \{M^{2n+}(aq)\}/\{MO_n\}\{H^+\} \tag{3.3}$$

where { } indicate activities of the species of interest. The equilibrium constant K_n in Equation (3.3) provides a quantitative measure of the amount of dissolution of a particular oxide. This quantity determines whether a particular oxide satisfies the condition of slow dissolution and if CBPC will form in a given pH range. Monovalent metal oxides with the exception of Ag_2O and Cu_2O (such as those of alkali metals) are soluble in water; divalent oxides are generally sparsely soluble; trivalent oxides are even less soluble (with few exceptions such as yttria and bismuth oxide); and higher valent oxides are mostly insoluble. Therefore, monovalent oxides dissolve rapidly in the phosphate solution and form phosphate precipitates without forming monolithic ceramics. Sparsely soluble divalent oxides are most suitable for the formation of well-crystallized ceramics. Tri- and quadrivalent oxides do not dissolve sufficiently; hence, it has been difficult to form ceramics by their dissolution. These observations imply that oxides should exhibit a certain low level of solubility if they are to form ceramics. The solubility should not be too high to form a precipitate or too low to react insufficiently.

To evaluate the impact of metal oxide solubility, it is useful to express the solubility constant (K_{sp}) in terms of a negative logarithm or $pK_{sp} = -\log K_{sp}$. For example, Pourbaix (1974) provides the following relationship for determining cation concentrations in acidic solution as a function of pH and pK_{sp}

$$\log \{M^{2n+}(aq)\} = pK_{sp} - 2n(pH) \tag{3.4}$$

Using this relationship, the aqueous solubility characteristics of several common divalent and trivalent oxides have been plotted as a function of pH in Figure 3.2 (from Wagh and Jeong 2003). For completeness of the solubility, profiles were extended into the alkaline region. Several conclusions may be drawn from Figure 3.2. For $pK_{sp} - 2n(pH) > 0$, $\{M^{2n+}(aq)\}$ will be very large, implying rapid dissolution of the oxide. For controlled dissolution of the oxide and to form a ceramic, $2n(pH)$ must be $\geq pK_{sp}$. Thus, the minimum pH (pH_{min}) for formation of a ceramic is given by $pH_{min} = pK_{sp}/2n$.

CaO does not satisfy this condition in the acidic region, and as a result it is not possible to form ceramics of Ca by an acid-base reaction. For this reason, hydroxyapatite ($Ca_5(PO_4)_3OH$), a major component of bone, is produced by an acid-base reaction between two sparsely soluble calcium phosphate salts such as tetracalcium phosphate ($Ca_4(PO_4)_2O$) and dibasic calcium phosphate ($CaHPO_4$) (Brown and Chow 1986). MgO comes close to satisfying this condition, but is still beyond the required pH range. As a result, formation of MgO ceramics has been possible only by reducing the reaction rate of MgO dissolution through calcination. FeO and ZnO are at the threshold of the range and it has been possible to form ceramics of these oxides often by calcination of ZnO. Trivalent oxides, such as Al_2O_3 and Fe_2O_3, satisfy the condition that $2n(pH)$ must be $\geq pK_{sp}$, but the solubility of Al_2O_3 and Fe_2O_3 is too low to form a ceramic.

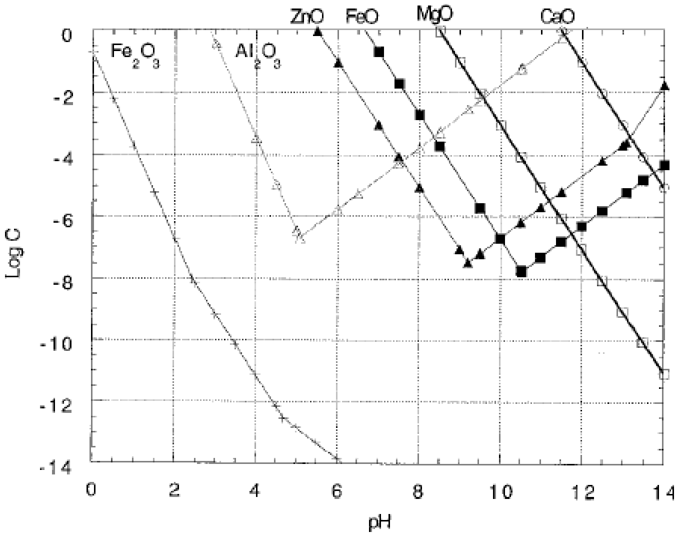


Figure 3.2. Aqueous Solubility Characteristics of Divalent and Trivalent Oxides as a Function of pH. Other solvents could form either labile or inert complexes with cation oxides (from Wagh and Jeong 2003).

Acid phosphates such as $NH_4H_2PO_4$, $(NH_4)_2HPO_4 \cdot 2H_2O$, and KH_2PO_4 have been used to form Mg-based phosphate ceramics. The pH of these phosphate salt solutions is 3.8, 2.3, and 4.1, respectively, at their saturation concentrations. These values are still lower than the pH_{min} needed for MgO, which implies there would be a spontaneous dissolution of MgO in the solutions of these phosphates. Calcination of MgO helps control its dissolution; however, despite this pretreatment only small-size ceramics can be formed with $NH_4H_2PO_4$ due to the low pH of the phosphate salt solution. A solution of $(NH_4)_2HPO_4$ with a sufficiently high pH of 7.2 may be used, but evolution of ammonia disrupts the formation of dense ceramics. Use of KH_2PO_4 does provide a high enough pH to form large-size ceramics that are dense and hard.

The requirement for formation of the aquosols (Figure 3.1b) is that the pH of the solution should be lower than the point of zero charge (PZC) of the oxide (Hunter 1981). Most of the divalent and trivalent metal oxides satisfy this condition in any acidic solution. For example, the PZCs for MgO, Al_2O, and Fe_2O_3 are 12.0, 8.6, and 9.0, and hence should form aquosols in an acidic solution. The PZC for quadrivalent oxides is lower in general and therefore are not good candidates for forming CBPCs in a moderately acidic solution. For example, silica—with a PZC of 2.5—will not form aquosols in an acidic solution, unless the solution is highly acidic. The case for many other quadrivalent oxides is similar.

For ceramic formation to be uniform, it is necessary that the aquosol is well distributed in the solution. It is well known that condensed phosphates are excellent dispersants and hence, these aquosols are well dispersed in phosphate solution. In addition, constant mixing of the slurry during formation of the ceramics also helps in dispersing these sols.

As in the case of the sol-gel process (Brinker and Scherer 1989), dissolution of oxides in an acidic solution and their subsequent reaction leads to formation of a gel. Initially, isolated sols are formed and they remain in a colloidal state, but as more and more cations are released into the solution, further condensation occurs and these sols become connected. As chains of sols are formed, they percolate throughout the solution to form the gel.

In the case of the sol-gel process, the objective is to produce stable sols and its gel; however, in the case of CBPCs, an unstable sol is required. The desired outcome for CBPCs is for the acid-base reaction to be initiated between the sols and the phosphate anions to form the corresponding hydrophosphate salt. In the case of divalent oxides, such as MgO, the acid-base reaction proceeds at room temperature and produces a room-temperature-setting ceramic. Thus, unstable sols will readily form a CBPC whereas stable ones do not. The gel is now converted to a saturated phosphate solution in which a significant amount of undissolved metal oxide particles remain and are uniformly distributed. The presence of undissolved metal oxide particles in the final ceramic is always detectable by XRD. As precipitation of the phosphates occur, these oxide particles form nuclei for crystallization and the entire gel condenses into a monolithic solid of CBPC. Thus, it is important that some unreacted particles are available to form a good stable ceramic. In addition to the crystalline phase, an amorphous phase is always detectable by XRD in these ceramics. Formation of this amorphous phase is dependent on the very fine particles that exist in the starter powders that dissolve completely in the acid solution, and also on the rate of dissolution of the oxide in the acid solution.

The dissolution rate of the oxides also plays a key role in the formation of ceramics. The rate of change of pH depends on the rate at which oxide powder is added to the solution during mixing; therefore, this is an external parameter that is controlled during operation. The rate will also depend on the surface morphology of the powder. Crystalline powders will dissolve more slowly than amorphous powders. Retardants (such as boric acid) have been used to reduce this rate. Retardants form unstable compounds that encapsulate the particles of the oxide powders and temporarily shield the grains from the acid solution, and retard the rate of availability of the oxides for dissolution (Sarkar 1991). Inasmuch as the condition for forming a ceramic requires that $2n(pH) \geq pKsp$, most of the heat is generated at pH_{min}. At higher pH, the heat evolution drops by a factor of 100 for each pH unit increase for divalent oxides, and by 1000 for trivalent oxides. Among the divalent oxides, CaO will produce the maximum heat, followed by MgO. This explains why it has not been possible to make a ceramic of calcium hydrophosphate and why MgO needs pretreatment or reduction of the reaction to form a ceramic.

Because of their high solubility and dissolution rate, commercially available oxides of Mg tend to react spontaneously with acid phosphates and form precipitates rather than forming ceramics. However, these same oxides, when calcined at high temperatures (nearly 1300°C), produce excellent ceramics. Eubank (1951) showed that calcination of MgO to 1300°C reduces porosity of individual grains and also increases particle size.

Further studies were conducted to determine the effect of calcination of MgO powder on its morphology and acid solubility (Wagh and Jeong 2003). Uncalcined commercial MgO powder was calcined at 1300°C for 3 hours and lightly crushed. Comparison of grain surfaces of the uncalcined powder with those of calcined MgO using SEM image analysis indicated that the uncalcined powder is covered with a powdery or microcrystalline substance whereas the same surface of the calcined powder is smooth, indicating reduction of the amorphous coating on the individual grains by crystallization. The particles of calcined powder also appeared bigger, indicating some grain growth due to the calcination process. The density of the calcined powders was increased from 3.36 to 3.57 g/cm^3, while the surface area was reduced from 33.73 to 0.34 cm^2/g. This significant reduction in surface area is the reason for the reduction in the solubility of the MgO powder. XRD analysis also indicated an increase in crystallinity for the calcined powders.

To investigate the effect of calcination of the MgO powder on its solubility, a dissolution study in H_3PO_4 solution was conducted (Wagh and Jeong 2003). The change in pH as a function of time for both calcined and uncalcined MgO powders is shown in Figure 3.3. During the first 10 minutes, the pH of the solution of uncalcined MgO increased from 1.5 to 5, whereas that of the calcined MgO increased from 1.5 to only 2. Initially, the rate of change of pH for uncalcined MgO is extremely sharp, but within minutes is reduced dramatically. The rate of change of pH for calcined MgO is small but significant and virtually constant. The very high initial rate of pH change for uncalcined powder is due to dissolution and subsequent reaction of amorphous MgO. The reaction products in this case will coat individual grains and prevent further dissolution of the powder. Once calcined, this amorphous MgO crystallizes and reduces the early rate of dissolution, allowing a slow but constant rate of dissolution throughout the test period. These observations explain why the solubility of calcined MgO is reduced and why calcined powder reacts slowly during formation of the phosphate ceramic.

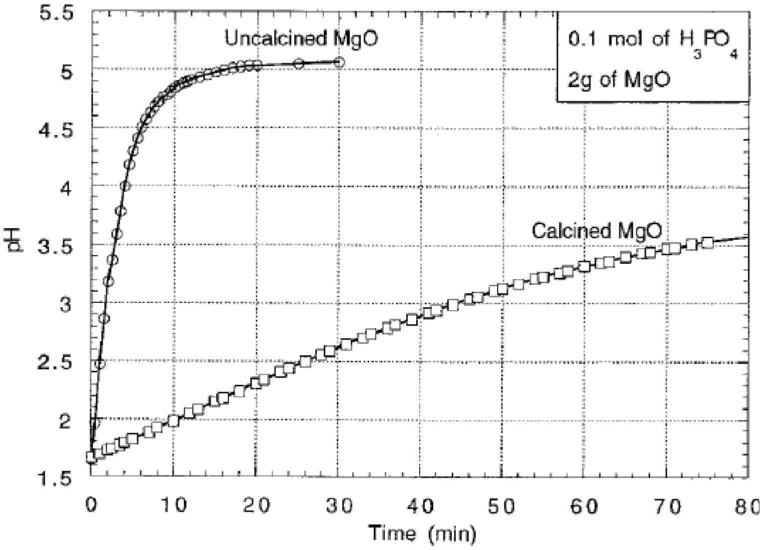


Figure 3.3. Increase in pH with Time During Neutralization of Calcined and Uncalcined MgO (from Wagh and Jeong 2003)

In large batches, the mixing time is only a few minutes before the exothermic acid-base reaction begins between MgO and H_3PO_4 or an acid phosphate, even with precalcined powders. Therefore, chemical retardants are needed in large-scale mixing operations (Sakar 1991). Boric acid is used for this purpose. When small quantities of boric acid (<1% of MgO) is added to the mixture, a coating develops on the MgO particles and retards early dissolution and delays the acid-base reaction. Sarkar (1991) studied the kinetics of reaction between MgO and ammonium phosphate in the presence of boric acid and reported that boric acid aids the development of a polymeric coating on the MgO grains and thus retards the setting rate. Wagh and Jeong (2003) conducted XRD and DTA to identify the phase of the coating on phosphate ceramics that formed during reaction between MgO and H_3PO_4 when 1 wt.% boric acid was added. Addition of the boric acid retarded the reaction time from 1.5 to 4.5 h. The polymeric coating on the MgO particles was identified as lunebergite ($Mg_3B_2(PO_4)_2(OH)_6{\cdot}6H_2O$) using XRD and confirmed by DTA. Identification of this phase implies the following mechanism for retardation of the reaction. When boric acid-containing MgO is mixed into the phosphate solution, lunebergite forms on the grains of the MgO as a coating. This prevents dissolution of the grains in the acid solution. Subsequently, as the pH of the solution rises, the coating slowly dissolves back into the solution and exposes the grains to the acid solution.

4.0 Ceramicrete Production Description

Ceramicrete fabrication steps and processing equipment needs are simple with low overall processing costs. Ceramicrete fabrication and processing equipment needs are very similar to those used for production of cement waste forms. Fabrication is conducted at room temperature and the entire stabilization reaction occurs within hours. The short setting time is particularly advantageous for radioactive wastes because it minimizes worker exposure. The raw materials required for fabricating the waste forms are readily available at comparatively low cost.

As input to the low-temperature immobilization study of potential secondary waste forms including Ceramicrete (Russell et al. 2006), CH2M HILL developed a concept for a standalone facility for implementing the Ceramicrete process for Hanford secondary liquid wastes. The following summarizes that concept.

4.1 Ceramicrete Process Description

The main steps in the Ceramicrete concept for Hanford secondary liquid wastes include

1. Liquid waste receipt
2. Partial neutralization
3. Getters and reducing agent addition
4. Partial dewatering by evaporation
5. Mixing waste solution and Ceramicrete dry materials
6. Waste form curing and storage

Figure 4.1 shows the conceptual flow diagram to implement this process. The liquid secondary wastes would be received into one of two tanks. One of the tanks is used to receive the wastes while the other is transferring its contents to the neutralization vessel.

In the neutralization tank, phosphoric acid is added to neutralize the caustic secondary wastes to a pH of approximately 5. The neutralization step is exothermic and the resulting heat will need to be dissipated. This neutralization step may or may not be necessary in the process. In more recent laboratory testing with simulated Hanford secondary wastes, the neutralization step is not included. Following the neutralization step, if used, stannous chloride ($SnCl_2$) is added to reduce technetium to the less mobile +4 oxidation state, and silver zeolite is added to capture iodine within the zeolite cage structure.

The next step is to dewater the aqueous waste solution using a vacuum evaporator. This step is intended to minimize the volume of the final Ceramicrete waste form. The extent of evaporation would have to be optimized with respect to equipment and energy costs relative to the savings in materials and disposal costs. Two evaporator condensate tanks are included to allow for one vessel to be sampled and discharged while the other is receiving the evaporator condensate.

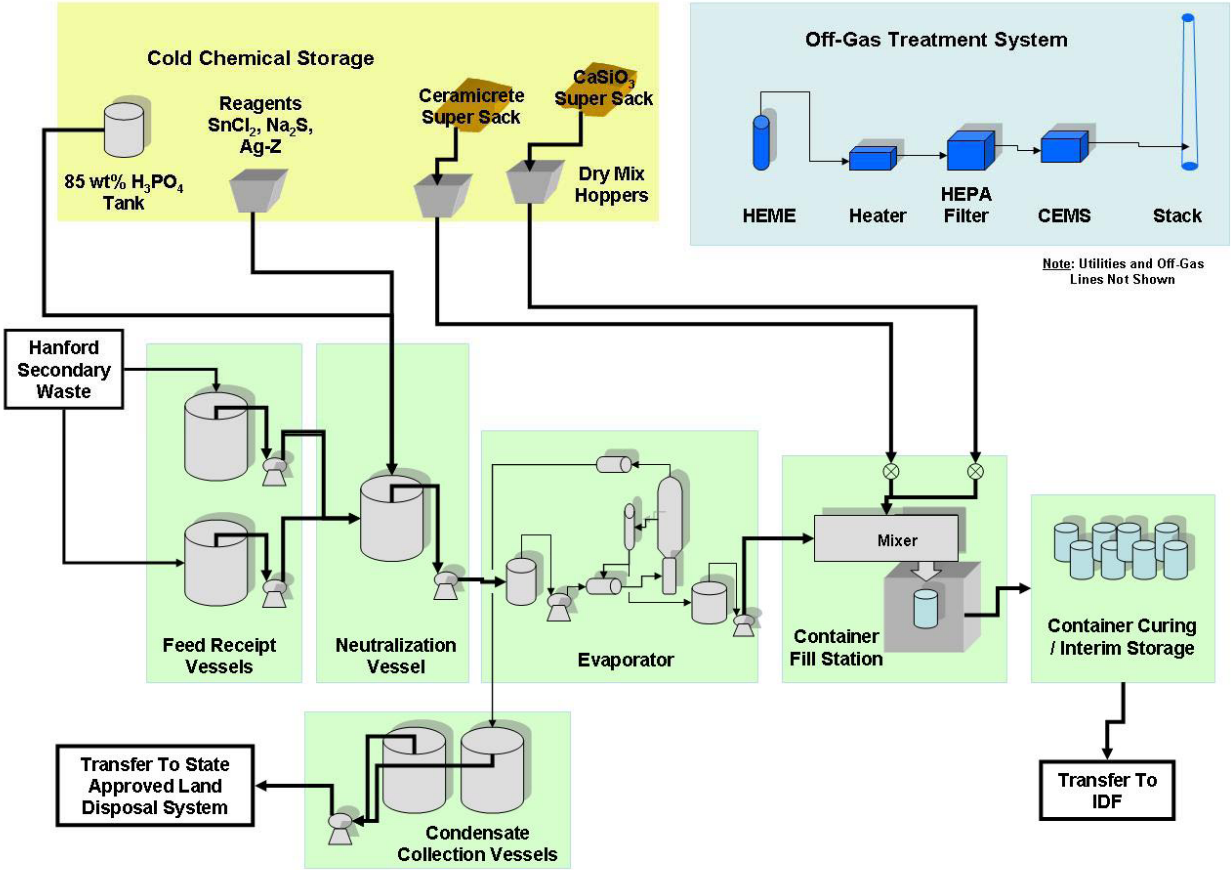


Figure 4.1. Conceptual Flow Diagram for Ceramicrete Process (from Russell et al. 2006)

The concentrated waste solution is then transferred to a mixer for blending the with the Ceramicrete dry materials including the magnesium oxide, mono potassium phosphate, and filler material. The ingredients are mixed in a batch in a mixer and are discharged into the waste form container. Mixing times are on the order of 20 to 30 minutes. The mixer is sized delivery to a single waste form container volume. A 2.04 m^3 box is proposed as a compromise between minimizing the number of containers produced on a daily basis and allowing for heat dissipation during the Ceramicrete curing process.

The Ceramicrete should set within a couple of hours and should be cured within 24 hours although heat dissipation may take longer depending on the size of the containers. Storage will be needed for the curing process and interim storage will be needed until the containers can be received in IDF.

Ancillary systems include chemical storage for the dry materials including the getters and Ceramicrete ingredients and a storage tank for the phosphoric acid for neutralizing the caustic secondary wastes. An off gas treatment system would also be required.

4.2 Equipment List and Sizing

As part of their Ceramicrete facility concept, CH2MHILL provided an equipment list for the major equipment components (Russell et al. 2006). The equipment is sized to process a maximum volume of

800,000 liters of 2M sodium secondary waste solution every 30 days with a 70 percent total operating efficiency. All vessels are sized to hold their contents at 85 percent capacity. Table 4.1 provides the equipment list and vessel sizes.

Table 4.1. Major Equipment List for Conceptual Ceramicrete Facility (from Russell et al. 2006)

Equipment	Quantity	Maximum Capacity
Waste Receipt Vessel (stainless steel)	2	4000 gal
Transfer Pump	2	100 gpm
Phosphoric Acid Storage Tank (carbon steel)	1	200 gal
Transfer Pump	1	0 to 5 gpm
Neutralization/Getter Addition Vessel (stainless steel)	1	2,200 gal
Transfer Pump	1	100 gpm
Dry Getter Material Hopper (carbon steel)	3	100 gal
Pneumatic Transfer	3	0.5 to 2 kg/mimute
Evaporator Feed Vessel (stainless steel)	1	500 gal
Transfer Pump	1	0 to 10 gpm
Evaporator Concentrate Vessel (stainless steel)	1	500 gal
Transfer Pump	1	0 to 10 gpm
Evaporator – Reboiler (stainless steel)	1	TBD BTU/hour
Vapor-Liquid Separator Vessel	1	1000 gal
Recirculation Pump	1	~10,000 gpm
Concentrate Pump	1	0 to 10 gpm
Primary Condenser	1	TBD BTU/hour
Secondary Condenser	1	TBD BTU/hour
Process Condensate Vessel (stainless steel)	2	5,300 gal
Transfer Pump	2	100 gpm
Dry Filler Material Hopper (carbon steel)	1	1,000 gal
Pneumatic Transfer	1	0 to 6 kg/minute
Ceramicrete Pre-Mix Hopper (carbon steel)	1	3,300 gal
Pneumatic Transfer	1	0 to 20 kg/minute
Ceramicrete Ribbon-Type Mixer (carbon steel)	1	2.04 m^3/batch
Container Storage Area with Overhead Crane	1	36 containers
Underground Pipeline		4,500 ft
Dust Bag House	1	TBD
Process Off-Gas Treatment System	1	TBD
Facility Off-Gas Treatment System	1	TBD
Distributive Control System	1	N/A
Office/Control Room Area	1	1,000 ft^2

4.3 Existing Facilities and Cost Data

Currently, there are no pilot-scale or full-scale Ceramicrete plants either under construction or in operation. Therefore operation costs are not available.

Schwinkendorf and Cooley (1999) conducted an economic evaluation of various treatment technologies available for mixed wastes in the DOE complex. It was concluded that Ceramicrete is one of the most economical methods currently available to treat these wastes. The material costs for Ceramicrete are about 50% higher than Portland cement (Wagh et al. 1999a).

Construction costs for the conceptual process design for the Ceramicrete Treatment Facility (CTF) described in the previous section were estimated by CH2MHILL. Based on this conceptual design, the estimated cost for construction of the CTF for immobilizing HSW was estimated to be $48.5 million (in 2005 dollars). Table 4.2 lists the major cost elements. Additional details are provided in the Russell document.

Table 4.2. Estimated Construction Costs for a Hanford Ceramicrete Facility (from Russell et al. 2006)

Cost Element	Cost (2005 $)
Other Project Costs	$7.852M
Engineering Support	$0.687M
Design	$2.410M
Procurement	$8.363M
Installation	$12.359M
Readiness / Startup	$0.669M
Subtotal	$32.340M
Contingency (50 Percent)	$16.170M
Total	**$48.510M**

5.0 Ceramicrete Physical Properties

In this section, physical properties measurements of the Ceramicrete waste form are discussed. Properties discussed include heat of reaction, porosity, and density.

5.1 Heat of Reaction

The enthalpy of reaction for equation 1 is exothermic with 66.8 kJ/mol ($MgKPO_4{\cdot}6H_2O$) of heat released during the reaction (Singh et al. 2006). The release of heat as a result of this reaction must be considered when designing the size and geometry of the waste form such that excessive heating of the waste form does not occur during the ceramic setting process. As indicated in Section 4.0, Ceramicrete waste forms fabricated at the 55-gal scale resulted in a maximum temperature increase of 82°C (Wagh et al. 2001).

5.2 Porosity and Density

Selected density and porosity measurements conducted on Ceramicrete waste forms are shown in Table 5.1. Data in the table are from waste forms fabricated with liquid waste streams that have similar compositions, at least in some respects, to expected HSW compositions as well as recent data for waste forms fabricated with WTP secondary waste stream simulants (Singh et al. 2011). Data compiled in the table that have both density and porosity measurements include waste forms made with the MKP binder only (Wagh et al. 1999a), Hanford Site tank supernatant waste simulant (Wagh et al. 2003), and ^{99}Tc eluent waste simulant (Singh et al. 2006). Additional data for which only density measurements are available include the following:

- waste forms made with surrogate salt waste (Wagh et al. 2001)
- WTP HSW simulant and Idaho Nuclear Technology and Engineering Center (INTEC) sodium-bearing waste (SBW) simulants (Russell et al. 2006)
- Hanford Site tank supernatant waste and Mayak supernatant waste simulant (Vinokurov et al. 2009)
- Waste forms fabricated with WTP secondary waste stream simulants (Singh et al. 2011).

The range in density observed for these waste forms ranged from 1.64 to 2.08 g/cm^3. The density of the MKP binder itself with no waste was 1.7 g/cm^3. The porosity range for the limited measurements made on the waste forms was 4.0% to 7.9%. The porosity of the MKP binder itself was 2.9%. These measurements indicate that addition of waste to the MKP binder results in an increase in both density and porosity.

Table 5.1. Porosity and Density Measurements of Ceramicrete Waste Forms

Waste Type/Loading	Actual Waste/Simulant/Spikes	Density (g/cm^3)	Porosity %	Reference
None	$MgKPO_4 \cdot 6H_2O$ binder only, no waste	1.7	2.9	Wagh et al. (1999a)
Surrogate salt waste ($NaNO_3$ and NaCl), 58 and 70 wt.% loading	Both NO_3^- and Cl^- wastes contained Fe_2O_3, $Al(OH)_3$, Na_3PO_4, Ca_2SiO_4, and water as major components, NaCl, $CaSO_4$, and $NaNO_3$ as salts; and Pb Cr, Hg, Cd, and Ni (up to 800-900 ppm) as heavy metals in each of the contaminant oxides, tricloroethylene	1.7–2.0		Wagh et al. (2001)
Hanford tank supernatant waste simulant, 39.8 wt.% loading	17 wt.% Na, 11.5 wt.% NO_3^-, pH=13.7, Cs, Ba, Re, Cd (2.3 ppm), Cr (938 ppm), Ag (11.5 ppm), Pb (37 ppm), and Zn (7.04 ppm)	1.88	7.9	Wagh et al. (2003)
^{99}Tc eluent waste simulant with $SnCl_2$ stabilization, 36 wt.% loading	1 M NaOH, 1 M ethylenediamine, 0.005 M Sn(II), 20–150 ppm Tc	1.8	4	Singh et al. (2006)
WTP HSW simulant, 25.8 wt.%	Na (45.2 g/L), CO_3^{-2} (60 g/L), NO_3^- (1.12 g/L), OH (1.6 g/L), TOC (13.9 g/L), Al (0.32 g/L), Cr, Ag, Cd, Re, I, Hg, Pb	2.06		Russell et al. (2006)
INTEC SBW simulant, 47.4 wt.%	Na (43.2 g/L), NO_3^- (269 g/L), Al (17.8 g/L), SO_4^{-2} (5.15 g/L), Ca (1.46 g/L), K (6.8 g/L), Cl^- (1.15 g/L), F^- (0.83 g/L), B, Mg, Cr, Mn, Fe, Cd, Cs, Ce, Hg, Pb, Re, I	2.02		Russell et al. (2006)
Hanford tank supernatant waste simulant, 35 wt.% loading	256 g/l Na, 168 g/L NO_3^-, 113 g/L NO_2^-, 83.7 g/L OH^-, CO_3^{-2}, Al, Cl^-, Cs, Sr, SO_4^{-2}, Cr, Pb, Cd, K, Am, Ce, Pu, Np, Am, Sr, Cs, Tc, I, Se	1.6–1.7		Vinokurov et al. (2009)
Mayak supernatant waste simulant, 43 wt.% loading	296 g/l Na, 99 g/L NO_3^-, 38 g/L NO_2^-, 91.5 g/L OH^-, Al, Cl^-, SO_4^{-2}, Cr, Cs, Sr, Tc, I, Se	1.8		Vinokurov et al. (2009)
WTP secondary waste simulant, baseline	1 M Na, 0.398 M OH^-, 0.328 M NO_3^-, 0.0939 M Al, 0.0939 TOC, 0.0228 M CO_3^{-2}, 0.0225 M Cl^-, 0.012 M NO_2^-, Si, K, PO_4^{-3}, SO_4^{-2}, F^-, Cr, Ag, As, Cd, Hg, Pb, Tc, I	1.84-2.07		Singh et al. (2011)

Table 5.1. (contd)

Waste Type/Loading	Actual Waste/Simulant/Spikes	Density (g/cm^3)	Porosity %	Reference
WTP secondary waste simulant, cluster 1	1 M Na, 0.435 M OH^-, 0.190 M NO_3^-, 0.114 M Al, 0.114 M TOC, 0.0466 M CO_3^{-2}, 0.0217 M Cl^-, 0.0105 M NO_2^-, Si, K, PO_4^{-3}, SO_4^{-2}, F^-, Cr, Ag, As, Cd, Hg, Pb, Tc, I	1.83-2.08		Singh et al. (2011)
WTP secondary waste simulant, cluster 2	1 M Na, 0.397 M NO_3^-, 0.245 M OH^-, 0.0922 M Al, 0.0922 M TOC, 0.0394 M CO_3^{-2}, 0.0383 M, 0.0291 M Cl^-, Si, K, PO_4^{-3}, SO_4^{-2}, F^-, Cr, Ag, As, Cd, Hg, Pb, Tc, I	1.72-2.08		Singh et al. (2011)
WTP secondary waste simulant, mixed waste	1.13 M NO_3^-, 1 M Na, 0.441 M NH_4, 0.0424 M Al, 0.0424M TOC, 0.0431 M NO_2^-, 0.0436 M SO_4^{-2}, 0.0287 M K, 0.0139 M Si, 0.0104 M CO_3^{-2}, 0.0104 M Cl^-, OH, Si, PO_4^{-3}, F^-, Cr, Ag, As, Cd, Hg, Pb, Tc, I	1.64-2.08		Singh et al. (2011)

6.0 Ceramicrete Performance

Actual secondary waste streams will not be generated until the WTP is functioning. As a result, no waste forms with actual secondary wastes can be tested at this time. Recently, a study was completed on the performance of Ceramicrete waste form fabricated with WTP secondary waste stream simulants (Singh et al. 2011). In addition to this study, a number of studies have been published previously on the performance of Ceramicrete for stabilizing many waste constituents that will occur in secondary waste. Studies particularly useful for evaluating the performance of Ceramicrete with wastes streams that are similar to secondary waste streams are briefly summarized below.

Investigations of the effectiveness of Ceramicrete for various surrogate wastes, including one intended to represent the salt waste inventory within the DOE complex, have been reported by Wagh et al. (2001). The surrogate wastes used in these studies contained Fe_2O_3, $Al(OH)_3$, Na_3PO_4, synthetic calcium silicate, and water as the major components; NaCl, $CaSO_4$, and $NaNO_3$ as the salts; and Pb, Cr, Hg, Cd, and Ni (up to 800–900 ppm) as the heavy metals in each of the contaminant oxides. Trichloroethylene was added to investigate if residual organics in the waste had any effect on the setting of the ceramic. The waste forms were fabricated at two waste loadings (58 and 70 wt.%) for each of the waste streams. TCLP leaching results demonstrated the hazardous contaminants were chemically immobilized and physically encapsulated within the Ceramicrete matrix. Density and compression strengths measured in the waste forms were also excellent.

Wagh et al. (2003) investigated stabilization of Hanford Site tank supernate simulants with Ceramicrete. The supernatant simulant contained 17% Na, 11.5% NO_3^-, Ag, Cd, Cr, Cs, Pb, Zn, and Re as a surrogate for ^{99}Tc, and a pH of 13.7. At a waste loading of 40%, it was demonstrated this waste stream was effectively stabilized.

Singh et al. (2006) studied the effectiveness of Ceramicrete for immobilizing ^{99}Tc in a waste stream that is generated by a process for separating ^{99}Tc from Hanford Site tank supernatant. A typical composition of this waste solution is 1 M NaOH, 1 M ethylenediamine, 0.005 M Sn(II), and Tc as high as 150 ppm or 0.0015 M. Two approaches were used to test Ceramicrete with this waste. In the first approach, the aqueous waste was stabilized directly by adding 38 wt.% fly ash and 2 - 3 wt.% $SnCl_2$ to the Ceramicrete binder. The optimal waste loading was 36 wt.%. The concentrations of ^{99}Tc in these waste forms ranged from 20 to 150 ppm. In the second approach, the role of $SnCl_2$ was investigated by adding $SnCl_2$ to precipitate ^{99}Tc from the waste solution prior to fabricating the waste form. In this approach, the ^{99}Tc concentrations in the waste forms were as high as 900 ppm. The waste forms were prepared in an anoxic nitrogen atmosphere. The performance of the waste forms was determined through various strength, leaching, and durability tests. Test results indicated that ^{99}Tc was effectively stabilized in the Ceramicrete and the waste form was durable in an aqueous environment.

Russell et al. (2006) conducted a study to evaluate low-temperature technologies to immobilize mixed radioactive and hazardous waste. Specific target wastes for immobilization were 1) WTP HSW and 2) INTEC SBW. Three waste forms were studied including an alkali-aluminosilicate hydroceramic cement, Ceramicrete phosphate-bonded ceramic, and DuraLith alkali-aluminosilicate geopolymer. The waste forms were fabricated using simulants of a Hanford Site secondary waste and INTEC SBW. The resulting waste forms were characterized with respect to the TCLP, compressive strength tests (both irradiated [total exposure of 1×10^8 rad] and as-received samples), durability (American National Standards Institute [ANSI]/ANS) 16.1 leachability index [ANS 1986]), and modified PCT.

Results reported in Russell et al. (2006) indicate that Ceramicrete met the TCLP Universal Treatment Standard in 40 CFR 268.48 for Cr, Cd, Ag, Hg, and Pb by more than an order of magnitude and the 3.45 MPa compressive strength criteria by about an order of magnitude (radiation exposure made no difference in the strength). For the PCT using the standard sample preparation process, there was evidence the samples may be dissolving or otherwise breaking up during the wash step before the test itself was started. Russell et al. (2006) indicate that further work would be necessary to understand the waste-form behavior in the PCT, and to interpret the results with respect to waste-form performance in a disposal facility. Results of the ANSI/ANS 16.1 leachability index test method (ANS 1976) met the leachability index requirement for Na (LI>6). Rhenium (used as a surrogate for Tc) in waste forms fabricated with either of the two waste stream simulants did not meet the target index (LI>11), and no I was detected in the leachate. Additional waste forms prepared with HSW spiked at Re and I concentrations above the nominal simulant concentrations resulted in leachability indices of better than 11.0. It was concluded that based on the TCLP, compressive strength, and Na leachability index requirements that Ceramicrete showed potential as an effective low temperature immobilizing waste; however, its effectiveness for immobilizing relatively volatile radionuclides, including ^{99}Tc and ^{129}I, could not be assessed without further testing. The ANSI/ANS 16.1 immersion test also revealed formulation issues that need to be addressed. Additional work has been performed to address these issues (Singh et al. 2011).

Performance of MKP waste forms fabricated with HLW simulants has been reported by Vinokurov et al. (2009). The wastes that were investigated include HLW simulants intended to represent liquid supernatants and sludges from Hanford Site tanks and Mayak (Russia). Novel procedures of solidification of HLW simulants were developed to increase stability of the MKP matrices to leaching radionuclides (Pu, Np, Am, Cs, Sr, Tc, I, and Se), matrix-forming (K, Mg, and PO_4) and admixture components (NO_3, NO_2, Na, and others) as well as hazardous elements (Pb, Cr, Zn, and others) according to the ANS, PCT, and TCLP standards. Density (~1.7 g/cm^3), compressive strength (>20 MPa), radiation resistance of the matrices, and chemical yield of radiolytic hydrogen (0.004 molecule H_2/100 eV) were determined.

In another study, Ceramicrete waste forms were fabricated using high concentrations (25 g/dm^3) of metal [Cd(II), Cr(III), Cu(II), Ni(II), Pb(II), and Zn(II)] nitrate solutions (Buj et al. 2009, 2010). Metal leachability and waste form strength tests indicated that in all cases the metals were effectively stabilized.

In a recently published document (Singh et al. 2011), Ceramicrete waste forms were fabricated with four WTP secondary waste effluent simulants and tested for physical properties and performance. The four WTP secondary waste effluent simulants used were baseline caustic scrubber, low salt, high salt, and mixed (caustic scrubber blended with 10% submerged bed scrubber waste stream). The baseline, cluster 1, cluster 2, and mixed waste streams are referred to as “B,” “C1,” “C2,” and “M,” respectively. Various Ceramicrete waste form formulations were produced by varying the quantities of the base ingredients, type, and quantities of powder fillers and additives, and waste loadings. Powder fillers used include class C fly ash, calcium silicate (wollastonite), and blast furnace slag. Additives used include boric acid, tin chloride ($SnCl_2$), Ag-loaded zeolite, and potassium sulfide (K_2S). Specific compositional details of the individual waste forms are available in Singh et al. (2011).

Further details of the results discussed above are provided in Sections 5.0 and 7.0.

7.0 Waste Acceptance Criteria

7.1 Void Space

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

7.2 Surface Dose Rate

Proposed dose rate limits for wastes to be accepted into the IDF include a constraint that containers have surface dose rates less than or equal to 2 mSv per hour (200 mrem per hour) at contact and less than 1 mSv per hour (100 mrem per hour) at 30 cm (11.8 in.) (RPP-8402 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 design of the facility (Fluor Hanford 2005). The dose rate calculation considered waste streams from the 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 or not the calculation included a container for the waste form block.

A dose rate of 1.25 mrem per hour (0.0125 mSv per hour) was calculated at 1 in. from the block side, and 0.75 mrem per hour (7.5 mSv per hour) was calculated at 1 ft 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

One of the IDF WAC requirements is the waste form shall contain no detectable free liquids as defined in SW-846 Method 9095. Because water introduced in the formulation or waste is bound as water of hydration, the Ceramicrete fabrication process does not produce free liquids when correctly formulated. If excessive water occurs in the waste stream, dewatering can be used to reduce waste volume; this can be done at 70ºC (Russell et al. 2006).

None of the waste forms fabricated with simulated WTP secondary waste had any observable free liquids (Singh et al. 2011). Free liquids were also not observed in any of the Ceramicrete waste forms fabricated with wastes that had compositions similar to secondary waste streams.

7.4 Dangerous Waste Limitations – Toxicity Characteristic Leaching Procedure

TCLP results for Ceramicrete waste forms fabricated with wastes relevant to secondary waste streams are shown in Table 7.1. These TCLP results include data compiled for waste forms made with Hanford Site tank supernatant waste simulant (Wagh et al. 2003); WTP HSW simulant and INTEC SBW simulants (Russell et al. 2006); and Hanford Site tank supernatant waste and Mayak supernatant waste simulant (Vinokurov et al. 2009). In all cases, the concentrations measured in the TCLP leachates were well below the Universal Treatment Standard limits. TCLP results for Ceramicrete waste forms fabricated with simulated WTP secondary waste streams are shown in Table 7.2 (Singh et al. 2011). Results with < indicate concentrations below the detection limit. The waste form compositions, simulated WTP secondary waste stream compositions, and waste loadings are available in (Singh et al. 2011). In all cases, the concentrations measured in the TCLP leachates were well below the Universal Treatment Standard limits. TCLP results for waste forms with fly ash had detectable levels of Cr and Se. Results for waste forms fabricated with mixed waste simulants, where appropriate amounts of Ag and Cd were present in the simulant, were below the detection limit. Pb was also below detection limit values. These results indicate that containments of RCRA metals are effective for all Ceramicrete formulations studied at metal concentrations.

7.5 Ignitibility

Because nitrate waste is ignitable, it is required that waste forms be nonflammable for safe transport and storage. Wagh et al. (2001) conducted ignitability tests on waste forms fabricated with surrogate salt waste containing nitrate using a procedure recommended by EPA (1995) to demonstrate that CBPC waste forms comply with this requirement. Results of the testing implied that salt waste solidified with CBPCs will not require any special packaging because their inorganic ceramic composition inhibits the spread of flames, indicating they are excellent solidification media for flammable salt waste.

7.6 Radiolysis

Radioactive fission product isotopes emit β and γ radiation while actinides also emit α radiation. When radioactive components are solidified within a waste form, self-radiation of the matrix can result in radiolysis of water or organic compounds present in the waste form. This can cause production of gases, such as hydrogen, that can result in pressurization of waste form containers during storage.

Wagh et al. (1999b) conducted a feasibility study of Ceramicrete stabilization of Rocky Flats Pu-contaminated ash. As part of this work, hydrogen generation was measured in waste forms containing various waste types and wt.% Pu (Table 7.3). Results indicate that the G value (quantity of H_2 generated per 100 eV of absorbed energy (assuming 100% of the decay energy is absorbed in the waste form) ranged from 0.10 to 31.8. Based on these results, Wagh et al. (1999b) determined that gas yield was minimal and did not result in pressurization of the waste container, concluding that hydrogen generation resulting from radiolytic decomposition of water and organic compounds in the waste was not a significant issue.

In a study of HLW immobilization in Ceramicrete, Vinokurov et al. (2009) measured radiolytic generation of hydrogen. Measurements were conducted on a waste form fabricated with 1.1 wt.% ^{239}Pu. During a 4-week period, the radiation absorbed dose of the waste form was 5.0×10^8 rad. The quantity of radiolytic hydrogen released was 0.004 H_2 molecules/100 eV.

Because significant quantities actinides are not expected to occur in the secondary waste stream, the impact of radiolysis on waste forms fabricated with secondary waste are expected to be much less than the above mentioned examples. Therefore, hydrogen generation resulting from radiolytic decomposition of water and organic compounds in Ceramicrete fabricated with secondary waste is not expected to be a significant issue.

Table 7.1. TCLP Results for Ceramicrete Waste Forms Fabricated with Wastes Relevant to Secondary Waste Streams

Waste Type/Loading	Actual Waste/Simulant/Spikes	Test Method	Component	Leachate Concentration (mg/L)	UTS Limit (mg/L)	Reference
Hanford tank supernatant waste simulant, 39.8 wt.% loading	17 wt.% Na, 11.5 wt.% NO_3^-, pH=13.7, Cs, Ba, Re, Cd (2.3 ppm), Cr (938 ppm), Ag (11.5 ppm), Pb (37 ppm), and Zn (7.04 ppm)		Cd	<0.01	0.11	Wagh et al. (2003)
			Cr	0.01	0.6	
			Ag	<0.05	0.14	
			Pb	<0.05	0.75	
			Zn	<0.05	4.3	
WTP HSW simulant, 25.8 wt.%	Na (45.2 g/L), CO_3^{-2} (60 g/L), NO_3^- (1.12 g/L), OH^- (1.6 g/L), TOC (13.9 g/L), Al (0.32 g/L), Cr, Ag, Cd, Re, I, Hg, Pb		Cr	0.0533	0.60	Russell et al. (2006)
			Cd	<0.00028	0.11	
			Ag	0.00779	0.14	
			Hg	<0.00766	0.025	
			Pb	0.00964	0.75	
INTEC SBW simulant, 47.4 wt.%	Na (43.2 g/L), NO_3^- (269 g/L), Al (17.8 g/L), SO_4^{-2} (5.15 g/L), Ca (1.46 g/L), K (6.8 g/L), Cl^- (1.15 g/L), F^- (0.83 g/L), B, Mg, Cr, Mn, Fe, Cd, Cs, Ce, Hg, Pb, Re, I		Cr	<0.0018	0.60	Russell et al. (2006)
			Cd	<0.00028	0.11	
			Ag	0.00345	0.14	
			Hg	<0.00766	0.025	
			Pb	0.00147	0.75	
Hanford tank supernatant waste simulant, 35 wt.% loading	256 g/L Na, 168 g/L NO_3^-, 113 g/L NO_2^-, 83.7 g/L OH, CO_3, Al, Cl, Cs, Sr, SO_4^{-2}, Cr, Pb, Cd, K, Am, Ce, Pu, Np, Am, Sr, Cs, Tc, I, Se	24 h agitation, extraction fluid no. 1, particle size <1 cm	Cs	<0.05		Vinokurov et al. (2009)
			Pb	0.005	0.75	
			Cr	0.04	0.60	
			Se	0.01	5.7	
			Cd	0.001	0.11	
			Zn	0.05	4.3	
			Cu	0.006		
			Co	0.001		
Mayak supernatant waste simulant, 43 wt.% loading	296 g/L Na, 99 g/L NO_3^-, 38 g/L NO_2^-, 91.5 g/L OH^-, Al, Cl^-, SO_4^{-2}, Cr, Cs, Sr, Tc, I, Se	24 h agitation, extraction fluid no. 1, particle size <1 cm	Sr	0.07		Vinokurov et al. (2009)
			Cr	0.2	0.60	
			Ni	0.5	11	

UTS = Universal Treatment Standard.

Table 7.2. TCLP Results on Ceramicrete Waste Forms Fabricated with WTP Secondary Waste Stream Simulants and Blank Samples (mg/l) (Singh et al. 2011)

Composition	As	Ba	Cd	Cr	Pb	Se	Ag	Hg
45FA Blank	0.183	<0.01	<0.01	0.375	<0.033	0.172	<0.01	<0.0007
45 CaSi Blank	<0.05	0.012	<0.01	0.014	<0.033	0.182	<0.01	<0.0007
35FA+10Slag Blank	0.074	0.011	<0.01	0.011	<0.033	0.268	<0.01	<0.0007
45FA+20WS(B)	0.15	<0.01	<0.01	0.013	<0.033	0.303	<0.01	<0.0007
45FA+15WS(B)	0.13	<0.01	<0.01	0.015	<0.033	0.129	<0.01	<0.0007
45CaSi+20WS(B)	<0.05	0.31	<0.01	0.016	<0.033	0.227	<0.01	<0.0007
45CaSi+15WS(B)	<0.05	<0.01	<0.01	0.019	<0.033	0.182	<0.01	<0.0007
35FA+10Slag+15WS(B)	0.15	<0.01	<0.01	0.016	<0.033	0.327	<0.01	<0.0007
35FA+10Slag+10WS(B)	0.14	0.01	<0.01	0.019	<0.033	0.397	<0.01	<0.0007
45FA+20WS(C1)	0.20	<0.01	<0.01	0.015	<0.033	0.262	<0.01	<0.0007
45FA+15WS(C1)	0.12	<0.01	<0.01	0.018	<0.033	0.457	<0.01	<0.0007
45CaSi+20WS(C1)	<0.05	<0.01	<0.01	<0.01	<0.033	0.226	<0.01	<0.0007
45CaSi+15WS(C1)	<0.05	<0.01	<0.01	0.011	<0.033	0.208	<0.01	<0.0007
35FA+10Slag+15WS(C1)	0.076	0.012	<0.01	0.020	<0.033	0.260	<0.01	<0.0007
35FA+10Slag+10WS(C1)	0.060	<0.01	<0.01	0.014	<0.033	<0.06	<0.01	<0.0007
45FA+20WS(C2)	0.14	0.011	<0.01	0.013	<0.033	0.297	<0.01	<0.0007
45FA+15WS(C2)	0.15	<0.01	<0.01	0.015	<0.033	0.173	<0.01	<0.0007
45CaSi+20WS(C2)	0.065	<0.01	<0.01	<0.01	<0.033	0.191	<0.01	<0.0007
45CaSi+15WS(C2)	<0.05	<0.01	<0.01	0.012	<0.033	0.085	<0.01	<0.0007
35FA+10Slag+15WS(C2)	0.31	0.019	<0.01	0.028	<0.033	0.398	<0.01	<0.0007
35FA+10Slag+10WS(C2)	0.25	0.013	<0.01	0.016	<0.033	0.283	<0.01	<0.0007
45FA+20WS(M)	0.096	0.011	<0.01	0.017	<0.033	0.267	<0.01	<0.0007
45FA+15WS(M)	0.182	<0.01	<0.01	0.011	<0.033	0.257	<0.01	<0.0007
45CaSi+20WS(M)	<0.05	<0.01	<0.01	0.0144	<0.033	0.219	<0.01	<0.0007
45CaSi+15WS(M)	<0.05	<0.01	<0.01	<0.01	<0.033	<0.06	<0.01	<0.0007
35FA+10Slag+10WS(M)	<0.05	<0.01	<0.01	0.011	<0.033	<0.06	<0.01	<0.0007
35FA+10Slag+15WS(M)	0.072	<0.01	<0.01	0.013	<0.033	0.138	<0.01	<0.0007
Universal Treatment Standard	**5**	**21**	**0.11**	**0.6**	**0.75**	**5.7**	**0.14**	**0.025**

Table 7.3. Radiolytic Hydrogen Generation in Ceramicrete Containing Various Concentrations of Pu (Wagh et al. 1999b)

Sample	Wt.% Pu	G Value (molecular H_2/100 eV)
CBPC containing U-Pu oxide mixture	5.245	0.13
CBPC containing TRU combustible residue	7.87	0.10
CBPC containing TRU combustible residue	5.00	0.23
CBPC containing TRU combustible residue and Bakelite compound	31.8	31.8

7.7 Pyrophoricity

Pyrophoricity is a property of metals and oxides of lower oxidation states, including radioactive elements, in which they spontaneously ignite during or after stabilization. An example of a pyrophoric component is Pu_2O_3. Oxidation to PuO_2 renders this element nonpyrophoric. It is not expected that any pyrophoric components of concern will occur at levels of concern in the secondary waste stream.

7.8 Compressive Strength

Compressive strength results for Ceramicrete waste forms fabricated with wastes relevant to secondary waste streams are shown in Table 7.4. The IDF WAC requirement for compressive strength is that the compressive strength of the waste form shall be at least 3.54×10^6 Pa (500 psi) when tested in accordance with ASTM C39/C39M.

These compressive strength results include data compiled for waste forms made with surrogate salt waste (Wagh et al. 2001); Hanford Site tank supernatant waste simulant (Wagh et al. 2003); ^{99}Tc eluent waste simulant (Singh et al. 2006); WTP HSW simulant and INTEC SBW simulants (Russell et al. 2006); Hanford Site tank supernatant waste and Mayak supernatant waste simulant (Vinokurov et al. 2009); and metal nitrate solutions (Buj et al. 2009). In all cases, the measured compressive strength exceeded the 3.54×10^6 Pa (500 psi) requirement.

Compressive strength data for Ceramicrete waste forms fabricated with simulated WTP secondary waste streams that were cured for periods of 16 to 96 days are shown in Tables 7.5–7.8 (Singh et al. 2011). The waste form compositions, simulated WTP secondary waste stream compositions, and waste loadings are available in (Singh et al. 2011). The only Ceramicrete waste form composition that did not meet the minimum compressive strength requirement for IDF waste acceptance (3.54E6 Pa, 500 psi) was 25FA+25W+1B.A fabricated with the mixed simulant. Compressive strengths of waste forms fabricated with baseline simulants at waste loadings of up to 20 wt.% had compressive strengths that were greater than 2500 psi. Compressive strengths generally increased with increasing cure times. Significantly lower compressive strengths were observed for waste forms containing 25 wt.% filler (fly ash or $CaSiO_3$) relative to 45 wt.% filler. Waste forms fabricated with cluster 1, cluster 2, and mixed wastes exhibited trends that were simular to those for the baseline wasteforms; however, the mixed waste forms exhibited a somewhat higher degree of scatter than the other wasteforms.

Table 7.4. Compressive Strength Results for Ceramicrete Waste Forms

Waste Type/Loading	Actual Waste/Simulant/Spikes	Preparation	Compressive Strength	Reference
Surrogate salt waste ($NaNO_3$ and NaCl), 58 and 70 wt.%	Both NO_3^- and Cl^- wastes contained Fe_2O_3, $Al(OH)_3$, Na_3PO_4, Ca_2SiO_4, and water as major components, NaCl, $CaSO_4$, and $NaNO_3$ as salts; and Pb Cr, Hg, Cd, and Ni (up to 800–900 ppm) as heavy metals in each of the contaminant oxides, trichloroethylene		1900 psi (13 MPa) NO_3 waste 1400 psi (9.7 MPa) Cl waste	Wagh et al. (2001)
Hanford tank supernatant waste simulant, 39.8 wt.% loading	17 wt.% Na, 11.5 wt.% NO_3^-, pH=13.7, Cs, Ba, Re, Cd (2.3 ppm), Cr (938 ppm), Ag (11.5 ppm), Pb (37 ppm), and Zn (7.04 ppm)		12–24 MPa	Wagh et al. (2003)
^{99}Tc eluent waste simulant with $SnCl_2$ stabilization, 36 wt.% loading	1 M NaOH, 1 M ethylenediamine, 0.005 M Sn(II), 20–150 ppm Tc		30 ± 7 MPa	Singh et al. (2006)
WTP HSW simulant, 25.8 wt.%	Na (45.2 g/L), CO_3^{-2} (60 g/L), NO_3^- (1.12 g/L), OH^- (1.6 g/L), TOC (13.9 g/L), Al (0.32 g/L), Cr, Ag, Cd, Re, I, Hg, Pb	21-day as-prepared (ANL) freeze-thaw cycling (ANL) no rad (PNNL) 10^8 rad (PNNL)	4076 psi (28.1 MPa) 2057 psi (14.2 MPa) 4870 psi (33.6 MPa) 5020 psi (34.6 MPa)	Russell et al. (2006)
INTEC SBW simulant, 47.4 wt.%	Na (43.2 g/L), NO_3^- (269 g/L), Al (17.8 g/L), SO_4 (5.15 g/L), Ca (1.46 g/L), K (6.8 g/L), Cl^- (1.15 g/L), F^- (0.83 g/L), B, Mg, Cr, Mn, Fe, Cd, Cs, Ce, Hg, Pb, Re, I	21-day as-prepared (ANL) freeze-thaw cycling (ANL) no rad (PNNL) 10^8 rad (PNNL)	4603 psi (31.7 MPa) 2230 psi (15.4 MPa) 5160 psi (35.6 MPa) 4910 psi (33.8 MPa)	Russell et al. (2006)
Hanford tank supernatant waste simulant, 35 wt.% loading	256 g/L Na, 168 g/L NO_3^-, 113 g/L NO_2^-, 83.7 g/L OH^-, CO_3, Al, Cl, Cs, Sr, SO_4, Cr, Pb, Cd, K, Am, Ce, Pu, Np, Am, Sr, Cs, Tc, I, Se	No irradiation and 2.8 × 10^8 rad (^{60}Co)	25–55 MPa	Vinokurov et al. (2009)
Mayak supernatant waste simulant, 43 wt.% loading	296 g/L Na, 99 g/L NO_3^-, 38 g/L NO_2^-, 91.5 g/L OH, Al, Cl^-, SO_4, Cr, Cs, Sr, Tc, I, Se	No irradiation and 2.8 × 10^8 rad (^{60}Co)	>20 MPa	Vinokurov et al. (2009)
Metal nitrate solutions	Cd, Cr(III), Cu, Ni, Pb, or Zn at 25 g/dm^3	Water-to-solid (W/S) ratio of 0.3 to 0.6 dm^3/kg	>3.45 MPa for all metals at W/S of 0.3 and 0.4 dm^3/kg	Buj et al. (2009)

Table 7.5. Compressive Strength (psi) for Ceramicrete Waste Forms Fabricated with WTP Simulated Secondary Waste (Baseline) (Singh et al. 2011)

Sample Composition	16–20 days		30–35 days		60 days	
	Average Compressive Strength (psi)	STDEV	Average Compressive Strength (psi)	STDEV	Average Compressive Strength (psi)	STDEV
45FA+20W	2698	1032	3203	691	4260	542
45FA+15W	2595	560	3755	1753	5583	347
45FA+10W	3239	175	4332	132	4568	857
45FA+5W	4479	616	4150	602	5555	1034
45FABlank	3680	1584	4582	1546	4189	376
25FA+25W	1113	415	1321	398	1582	292
25FABlank	1317	420	2351	438	1236	28
25FA+25W+1B.A.	1215	134	1358	42	1819	34
45CaSi+20W	4794	126	6196	1342	5901	192
45CaSi+15W	3968	300	5473	811	4994	92
45CaSiBlank	4423	651	5760	1029	5037	197
25CaSi+25W	2768	553	3152	968	2525	547
25CaSiBlank	3044	760	4454	1077	3218	442
35FA+10Slg+10W	3623	703	4834	1035	3727	1315
35FA+10SlgBlank	5378	266	7376	0	5682	2162
35FA+10Slg+15W	3076	314	4103	586	3019	996

Table 7.6. Compressive Strength (psi) for Ceramicrete Waste Forms Fabricated with WTP Simulated Secondary Waste (Cluster 1) (Singh et al. 2011)

	16–19 days		30–39 days		90–96 days	
Sample Composition	Average Compressive Strength (psi)	STDEV	Average Compressive Strength (psi)	STDEV	Average Compressive Strength (psi)	STDEV
45FA+20W	2275	485	4259	639	3799	1900.41
45FA+15W	3193	562	6477	0	3910	2201
45FA+10W	3960	1230	4820	687	4837.65	2366
45FA+5W	3075	733	4018	1395	3765	1297
45FABlank	3680	1584	4582	1546	NT	NT
25FA+25W	1631	180	1376	571	1533	465
25FABlank	1317	420	2351	439	NT	NT
25FA+25W+1B.A.	2242	702	2181	712	2122	171
45CaSi+20W	4712	615	3632	154	4391	954
45CaSi+15W	4381	985	4932	736	4672	790
45CaSiBlank	4423	651	5760	1029	NT	NT
25CaSi+25W	2873	268	3540	1477	3548	90
25CaSiBlank	3044	760	4454	1076	NT	NT
35FA+10Slg+10W	4806	585	5005	1146	4959	1131
35FA+10SlgBlank	5378	266	7376	0	NT	NT
35FA+10Slg+15W	2760	360	3503	791	2378	836

Table 7.7. Compressive Strength (psi) for Ceramicrete Waste Forms Fabricated with WTP Simulated Secondary Waste (Cluster 2) (Singh et al. 2011)

	21–30 days	
Sample Composition	Average Compressive Strength (psi)	STDEV
45FA+20W	4005	167
45FA+15W	4483	569
45FA+10W	3269	368
45FA+5W	2186	579
45FABlank	4582	1546
25FA+25W	1370	431
25FABlank	2351	439
25FA+25W+1B.Acid	840	224
45CaSi+20W	4950	355
45CaSi+15W	4230	868
45CaSiBlank	5760	1029
25CaSi+25W	2618	115
25CaSiBlank	4454	1076
35FA+10Slg+10W	4039	304
35FA+10SlgBlank	7376	0
35FA+10Slg+15W	2201	426

Table 7.8. Compressive Strength (psi) for Ceramicrete Waste Forms Fabricated with WTP Simulated Secondary Waste (Mixed) (Singh et al. 2011)

	16–20 days		30–40 days	
Sample Composition	Average Compressive Strength (psi)	STDEV	Average Compressive Strength (psi)	STDEV
45FA+20W	2403	720.64	4561	1907
45FA+15W	3577	1622	3892	1873
45FA+10W	3130	415	4299	1587
45FA+5W	3101	520	2626	756
45FABlank	3680	1584	4582	1547
25FA+25W	1874	249	–	–
25FABlank	1316	419	–	–
25FA+25W+1B.Acid	147	66	–	–
45CaSi+20W	3296	573	–	–
45CaSi+15W	4469	602	–	–
45CaSiBlank	4422	651	–	–
25CaSi+25W	2792	170	–	–
25CaSiBlank	3043	760	–	–
35FA+10Slg+10W	2631	1712	–	–
35FA+10SlgBlank	5378	266	–	–
35FA+10Slg+15W	1875	997	–	–

Compressive strength data for Ceramicrete waste forms fabricated with simulated WTP secondary waste streams that were immersed in water for periods of 16 to 90 days are shown in Tables 7.9–7.12 (Singh et al. 2011). For the un-immersed waste forms, the only waste form composition that did not meet the minimum compressive strength requirement for IDF waste acceptance (3.54E6 Pa, 500 psi) was 25FA+25W+1B.A fabricated with the mixed simulant and cluster 2 (30 day immersion only, 60 day and 90 day immersion tests were > 500 psi). Compressive strengths of water immersed samples were similar or even increased with immersion as compared to the as-fabricated samples for the same filler and waste loading for baseline, cluster 1 and mixed wastes. Cluster 2 waste forms exhibited a drop in strength with immersion time compared to the as-fabricated samples. Similar to the un-immersed samples, wastes forms with 25 wt.% filler and 25 wt.% waste loading exhibited low compressive strength.

Table 7.9. Compressive Strength (psi) for Ceramicrete Waste Forms Fabricated with WTP Simulated Secondary Waste (Baseline) Immersed in Water (Singh et al. 2011)

	(30 days H_2O Immersion)		(60 days H_2O Immersion)		(90 days H_2O Immersion)	
Sample Composition	Average Compressive Strength (psi)	STDEV	Average Compressive Strength (psi)	STDEV	Average Compressive Strength (psi)	STDEV
45FA+20W	3095	652	3354	376	3948	1645
45FA+15W	2974	51	3330	1238.92	3205	1868
45FA+10W	4102	666	4210	309	4173	663
45FA+5W	3049	676	2802	792	2944	702
45FABlank	3582	326	3088	839	3083	911
25FA+25W	1138	115	941	191	1325	308
25FABlank	900	160	1201	411	1401	85
25FA+25W+1B.A.	748	180	1431	276	NT	NT
45CaSi+20W	4299	578	3000	464	5051	537
45CaSi+15W	3943	333	4102	1110	4337	276
45CaSiBlank	3743	410	4412	611	4846	1124
25CaSi+25W	3434	170	3104	849	2995	1220
25CaSiBlank	2977	714	3709	877	2187	681
35FA+10Slg+10W	3784	1758	4531	927	NT	NT
35FA+10SlgBlank	2878	483	6117	853	4742	700
35FA+10Slg+15W	3393	87	2946	69	3084	1926

Table 7.10. Compressive Strength (psi) for Ceramicrete Waste Forms Fabricated with WTP Simulated Secondary Waste (Cluster 1) Immersed in Water (Singh et al. 2011)

	(30 days H_2O Immersion)		(60 days H_2O Immersion)		(90 days H_2O Immersion)	
Sample Composition	Average Compressive Strength (psi)	STDEV	Average Compressive Strength (psi)	STDEV	Average Compressive Strength (psi)	STDEV
45FA+20W	3167	924	2501	236	3307	465
45FA+15W	3840	1700	3788	838	3228	625
45FA+10W	3244	383	5349	642	4997	2114
45FA+5W	2500	3	3524	1432	2974	843
45FABlank	3582	326	3088	839	3083	911
25FA+25W	825	1	1093	210	603	293
25FABlank	900	160	1201	411	1401	85
25FA+25W+1B.A.	1465	263	2317	164	NT	NT
45CaSi+20W	3625	1656	2992	209	4371	1066
45CaSi+15W	2925	264	3874	754	3220	648
45CaSiBlank	3743	410	4412	611	4845	1124
25CaSi+25W	3170	918	2815	679	2550	294
25CaSiBlank	2977	714	3709	877	2187	681
35FA+10Slg+10W	3617	148	6734	1226	5597	2185
35FA+10SlgBlank	2878	483	6117	853	4742	700
35FA+10Slg+15W	3222	886	1808	1359	3523	777

Table 7.11. Compressive Strength (psi) for Ceramicrete Waste Forms Fabricated with WTP Simulated Secondary Waste (Cluster 2) Immersed in Water (Singh et al. 2011)

	(30 days H_2O Immersion)		(60 days H_2O Immersion)		(90 days H_2O Immersion)	
Sample Composition	Average Compressive Strength (psi)	STDEV	Average Compressive Strength (psi)	STDEV	Average Compressive Strength (psi)	STDEV
45FA+20W	2441	320	1612	299.27	2297	257
45FA+15W	3467	559	2695	126	2759	537
45FA+10W	1519	312	2124	35	2515	570
45FA+5W	2377	517	2272	264	2203	281
45FABlank	3582	326	3088	839	3083	911
25FA+25W	1180	120	1207	167	1178	97
25FABlank	900	160	1201	411	1401	85
25FA+25W+1B.Acid	456	155	615	204	841	223
45CaSi+20W	3868	290	3807	202	3234	643
45CaSi+15W	3594	489	4147	1098	4053	324
45CaSiBlank	3743	410	4412	611	4845	1124
25CaSi+25W	2400	891	1927	224	2402	800
25CaSiBlank	2977	714	4412	611	2187	681
35FA+10Slg+10W	2364	430	1973	783	2178	238
35FA+10SlgBlank	2878	483	6117	853	4742	700
35FA+10Slg+15W	1413	420	1477	403	1537	475

Table 7.12. Compressive Strength (psi) for Ceramicrete Waste Forms Fabricated with WTP Simulated Secondary Waste (Mixed) Immersed in Water (Singh et al. 2011)

	(30 days H_2O Immersion)		(60 days H_2O Immersion)		(90 days H_2O Immersion)	
Sample Composition	Average Compressive Strength (psi)	STDEV	Average Compressive Strength (psi)	STDEV	Average Compressive Strength (psi)	STDEV
45FA+20W	2598	586	3078	586	3174	1204
45FA+15W	2431	1590	3353	1590	2586	1100
45FA+10W	4030	1073	4625	1073	3266	484
45FA+5W	2879	797	2740	797	3966	1148
45FABlank	3582	326	3088	839	3083	911
25FA+25W	1976	376	4155	597	2472	548
25FABlank	900	160	1201	411	1401	85
25FA+25W+1B.Acid	19	33	242	113	196	63
45CaSi+20W	4062	7545	3912	782	3173	184
45CaSi+15W	3672	560	3551	923	3334	1443
45CaSiBlank	3743	410	4412	611	4845	1124
25CaSi+25W	1909	1110	1940	6	1774	1043
25CaSiBlank	2977	714	3709	877	2188	681
35FA+10Slg+10W	3315	153	1950	891	2672	648
35FA+10SlgBlank	2878	483	6117	853	4742	700
35FA+10Slg+15W	1896	903	2598	1082	1187	225

7.9 Leachability Index

Leachability data for Ceramicrete waste forms fabricated with wastes relevant to secondary waste streams are shown in Table 7.13. The leachability data are presented in terms of leachability index, diffusivity (ANSI/ANS-16.1, ANS [1986]), and leaching rate (PCT, ASTM [1997]).

The leachability index (LI) is defined as follows:

$$LI = -\log(D) \qquad (7.1)$$

where D is the effective diffusivity (cm^2/s).

Leachability index and diffusivity data available in Table 7.13 include results for waste forms made with surrogate salt waste (Wagh et al. 2001) and ^{99}Tc eluent waste simulant (Singh et al. 2006). Note that the ^{99}Tc eluent waste simulant samples were prepared in an anoxic (nitrogen) atmosphere and the leach tests were also conducted in an anoxic (nitrogen) atmosphere. Additional leachability index data in Table 7.5 include results for waste forms made with WTP HSW simulant and INTEC SBW simulants (Russell et al. 2006), and Hanford Site tank supernatant waste and Mayak supernatant waste simulant (Vinokurov et al. 2009).

PCT data available in Table 7.13 include results for waste forms made with Hanford Site tank supernatant waste simulant (Wagh et al. 2003); ^{99}Tc eluent waste simulant (Singh et al. 2006); WTP HSW simulant and INTEC SBW simulants (Russell et al. 2006); and Hanford Site tank supernatant waste and Mayak supernatant waste simulant (Vinokurov et al. 2009). In all cases, the leachability index and diffusivity results met or exceeded applicable standards. Applicable standards are not currently available for PCTs and results are included for information only.

Leachability data for Ceramicrete waste forms fabricated with simulated WTP secondary waste streams are shown in Table 7.14 (Singh et al. 2011). The results in Table 7.14 are for tests conducted for 60 days, except for the baseline samples (bold) that were conducted for 90 days. The waste form compositions, simulated WTP secondary waste stream compositions, and waste loadings are available in Singh (2011). The leachability data are presented in terms of leachability index (ANSI/ANS-16.1 [ANS 1986]). Leachant solutions were analyzed for the radioactive surrogates, I and Re, and Mg, Na, P, Si, and Ag. In most cases, these results met or exceeded applicable standards. Iodine was below the detection limit in all leachates. Using the detection limit of 5 ppb, the worst-case LI values for I ranged from >5.8 to >8.2. The LI values calculated for Re ranged from 7.9 to 9.0 with no specific trend found with waste simulant or filler type. LI values for Mg, P, and Si ranged from 8.3 to 12.6, indicating good durability for all the waste forms. The LI calculated for Na ranged from 7.6 to 10.4. The ANS 16.1 test results indicate that the waste forms effectively contain the radionuclide surrogates Re and I at simulant waste loadings as high as 20 wt.%.

It is noteworthy that that some degradation of the waste forms was observed in the samples post ANS 16.1 tests. Fine cracks were observed in samples with fly ash and $CaSiO_3$ filler. Samples with fly ash + slag filler showed the most pronounced cracking. Several explanations were given as possible reasons for the occurance of this cracking. The first possible explanation was that swelling of the zeolite beads over time may have caused cracking. It was also indicated that unreacted MgO powder in the waste could hydrate to form $Mg(OH)_2$ during the ANS 16.1 or water immersion tests causing swelling and cracking. Another possibility indicated was that because the waste simulants are rich in Na a reaction between the zerolite and the pore fluid could form hydous amorphous sodium silicate resulting in expansion and cracking. In spite of the cracks, release of radionuclide surrogates did not increase indicating chemical binding of the species in the waste form was effective.

7.10 Weight Loss Measurements

As part of the water immersion testing, weight loss measurements of Ceramicrete waste forms fabricated with simulated WTP secondary waste streams were made (Singh et al. 2011). These data, shown in Table 7.15, are not part of the IDF waste acceptance criteria but are included for data completeness. Weight loss for the samples was determined at 1, 2, and 3 month intervals. Results indicate the greatest weight loss occurs during the first month, with losses ranged from 5% to 15%. Subsequent weight losses were significantly less. Depending on the sample composition, the additional weight losses that occurred during the subsequent two months ranged from 2% to 3%. It appears that the waste forms fabricated with the $CaSiO_3$ filler exhibited slightly higher weight loss compared to other filler compositions. It was suggested that the weight loss was due to removal of unreacted binder powders at the surfaces of the waste forms (Singh et al. 2011).

Table 7.13. Leachability Index, Diffusivity (ANSI/ANS-16.1), and Leaching Rate Results (PCT, 90ºC except where noted) for Ceramicrete Waste Forms

Waste Type/ Loading	Actual Waste/ Simulant/Spikes	Leachability Index (LI) ANSI/ANS-16.1	Diffusivity (cm^2/s)	Normalized Leaching Rate (g/m^2 day) PCT	Reference
Surrogate salt waste ($NaNO_3$ and NaCl), 58 and 70 wt.%	Both NO_3^- and Cl^- wastes contained Fe_2O_3, $Al(OH)_3$, Na_3PO_4, Ca_2SiO_4, and water as major components, NaCl, $CaSO_4$, and $NaNO_3$ as salts; and Pb Cr, Hg, Cd, and Ni (up to 800–900 ppm) as heavy metals in each of the contaminant oxides, tricloroethylene	7.2 – NO_3^- (NO_3 waste, 58 wt.% loading) 8.9 – Cl^- (Cl waste, 58 wt.% loading)	6.31×10^{-8} NO_3^- waste (58 wt.% loading) 1.26×10^{-9} Cl^- waste (60 wt.% loading)		Wagh et al. (2001)
Hanford tank supernatant waste simulant, 39.8 wt.% loading	17 wt.% Na, 11.5 wt.% NO_3^-, pH=13.7, Cs, Ba, Re, Cd (2.3 ppm), Cr (938 ppm), Ag (11.5 ppm), Pb (37 ppm), and Zn (7.04 ppm)			Mg – 1.4×10^{-6} K – 0.009 P – 0.006 Na – 0.008 NO_3^- – 0.077	Wagh et al. (2003)
^{99}Tc eluent waste simulant with and without $SnCl_2$ stabilization, 36 wt.% loading	1 M NaOH, 1 M ethylenediamine, 0.005 M Sn(II), 20–150 ppm Tc. Prepared in anoxic (nitrogen) atmosphere and leach tests conducted in anoxic (nitrogen) atmosphere	8.92–Tc (20 ppm Tc) 8.53–Tc (40 ppm Tc) 11.54–Tc (20 ppm Tc+Sn) 11.27–Tc (40 ppm Tc+Sn) 14.42–Tc (124 ppm Tc+Sn) 14.6–Tc (41 ppm Tc_{pct}+Sn) 13.3–Tc (164 ppm Tc_{pct}+Sn) 14.6–Tc (903 ppm Tc_{pct}+Sn)	1.2×10^{-9}–Tc (20 ppm Tc) 2.95×10^{-9}–Tc (40 ppm Tc) 2.9×10^{-12}–Tc (20 ppm Tc+Sn) 5.4×10^{-12}–Tc (40 ppm Tc+Sn) 3.8×10^{-15}–Tc (124 ppm Tc+Sn) 2.2×10^{-14}–Tc (41 ppm Tc_{pct}+Sn) 2.3×10^{-13}–Tc (164 ppm Tc_{pct}+Sn) 7.2×10^{-15}–Tc (903 ppm Tc_{pct}+Sn)	25ºC 0.0039–Tc (40 ppm Tc_{pct}+Sn) 0.0085–Tc (164 ppm Tc_{pct}+Sn) 0.0011–Tc (903 ppm Tc_{pct}+Sn) 90ºC 0.072–Tc (40 ppm Tc_{pct}+Sn) 0.11–Tc (164 ppm Tc_{pct}+Sn) 0.036–Tc (903 ppm Tc_{pct}+Sn)	Singh et al. (2006)
WTP HSW simulant, 25.8 wt.%	Na (45.2 g/L), CO_3^{-2} (60 g/L), NO_3^- (1.12 g/L), OH^- (1.6 g/L), TOC (13.9 g/L), Al (0.32 g/L), Cr, Ag, Cd, Re, I, Hg, Pb	8.08, 8.20 – Na 7.02, 7.36 – Re >3.60, >3.60 – I 12.7- Re (CH2MHILL) 11.2 – I (CH2MHILL) (CH2MHILL work at 7 days and higher initial Re and I concentrations)		Na – 14.76, 14.76, 250, 284 K – 44.06, 42.62, 403, 427 Si – 0.240, 0.257, 8.81,6.64 Mg – 0.003, 0.002, 0.228, 0.119 P – 16.84, 16.51, 202, 203	Russell et al. (2006)

Table 7.13. (contd)

Waste Type/ Loading	Actual Waste/ Simulant/Spikes	Leachability Index (LI) ANSI/ANS-16.1	Diffusivity (cm^2/s)	Normalized Leaching Rate (g/m^2 day) PCT	Reference
INTEC SBW simulant, 47.4 wt.%	Na (43.2 g/L), NO_3^- (269 g/L), Al (17.8 g/L), SO_4^{-2} (5.15 g/L), Ca (1.46 g/L), K (6.8 g/L), Cl^- (1.15 g/L), F^- (0.83 g/L), B, Mg, Cr, Mn, Fe, Cd, Cs, Ce, Hg, Pb, Re, I	7.59, 7.56 – Na 7.41, 7.42 – Re >5.55, >5.54 – I		Na – 26.56, 28.08, 358, 360 K – 44.40, 45.11, 547, 539 Si – 0.335, 0.048, 1.20, 1.28 Mg – 0.008, 0.008, 0.538, 0.474 P – 7.08, 7.32, 92.5, 94.0	Russell et al. (2006)
Hanford tank supernatant waste simulant, 35 wt.% loading	256 g/L Na, 168 g/L NO_3, 113 g/L NO_2, 83.7 g/L OH, CO_3^{-2}, Al, Cl, Cs, Sr, SO_4^{-2}, Cr, Pb, Cd, K, Am, Ce, Pu, Np, Am, Sr, Cs, Tc, I, Se	^{237}Np – 12.8 ^{239}Pu – 13.5 ^{90}Sr – 10.9 ^{137}Cs – 11.4 ^{99}Tc – 9.9 ^{131}I – 11.2 ^{75}Se – 9.6		Mg – 6.6×10^{-5} K – 0.024 P – 0.0072 Na – 0.024 NO_3^- – 0.038 Zn – <0.012 Cr – 8.5×10^{-5} Ni – 7.0×10^{-5} Cd – 0.0018 Pb – 7.3×10^{-4}	Vinokurov et al. (2009)
Mayak supernatant waste simulant, 43 wt.% loading	296 g/L Na, 99 g/L NO_3^-, 38 g/L NO_2^-, 91.5 g/L OH^-, Al, Cl^-, SO_4^{-2}, Cr, Cs, Sr, Tc, I, Se	^{90}Sr – 11.1 ^{137}Cs – 13.0 ^{131}I – 7.9		Mg – 4.1×10^{-6} K – 0.019 P – 0.0063 Na – 0.017 NO_3^- – 0.031	Vinokurov et al. (2009)

Table 7.14. Leaching Index Results from ANS 16.1 Tests Conducted on Ceramicrete Waste Forms Fabricated with WTP Secondary Waste Stream Simulants and Blank Samples (Singh et al. 2011)

Sample	Waste Simulant	Mg	Na	P	Si	Ag	Re	I[(a)]
45FA+Blank	Blank	10.5	-	8.4	12.5	16.3	-	-
45FA+Blank	Blank	10.5	-	8.4	12.5	16.2	-	-
45FA+20WS(B)	**B**	**11.0**	**8.1**	**8.5**	**12.4**	**16.6**	**8.6**	**>6.5**
45FA+20WS(B)	**B**	**10.8**	**8.1**	**8.3**	**12.2**	**14.5**	**8.6**	**>6.5**
45FA+15WS(B)	**B**	**10.6**	**8.2**	**8.3**	**12.2**	**16.1**	**8.6**	**>6.2**
45FA+15WS(B)	**B**	**10.7**	**8.2**	**8.4**	**12.3**	**16.4**	**8.6**	**>6.2**
45CaSi+20WS(B)	**B**	**10.9**	**7.6**	**8.4**	**11.3**	**17.2**	**8.4**	**>6.6**
45CaSi+20WS(B)	**B**	**11.0**	**7.6**	**8.5**	**11.3**	**17.7**	**8.4**	**>6.6**
45CaSi+15WS(B)	**B**	**11.0**	**7.7**	**8.5**	**11.3**	**16.9**	**8.3**	**>6.2**
45CaSi+15WS(B)	**B**	**11.0**	**7.7**	**8.5**	**11.4**	**17.8**	**8.3**	**>6.3**
45CaSi+Blank	Blank	11.8	10.2	9.0	11.9	17.7	-	-
45CaSi+Blank	Blank	11.9	10.4	9.1	11.7	17.7	-	-
35FA+10Slag+15WS(B)	B	11.3	8.0	8.5	12.2	17.2	8.5	>6.3
35FA+10Slag+15WS(B)	B	11.3	8.0	8.5	12.2	17.1	8.5	>6.3
35FA+10Slag+Blank	Blank	11.5	9.6	8.8	12.2	17.2	-	-
35FA+10Slag+Blank	Blank	11.6	9.7	8.9	12.6	17.2	-	-
45FA+20WS(C1)	C1	9.4	8.0	8.4	12.3	16.0	8.7	>6.2
45FA+20WS(C1)	C1	11.1	8.0	8.4	12.3	16.1	8.8	>6.2
45FA+15WS(C1)	C1	10.7	8.0	8.3	12.2	16.1	8.6	>5.8
45FA+15WS(C1)	C1	10.7	8.0	8.3	12.2	16.8	8.6	>5.8
45CaSi+20WS(C1)	C1	11.2	7.6	8.5	11.8	17.4	8.1	>6.2
45CaSi+20WS(C1)	C1	11.2	7.6	8.5	11.6	17.5	8.1	>6.2
45CaSi+15WS(C1)	C1	11.3	7.6	8.6	11.7	17.7	8.0	>5.9
45CaSi+15WS(C1)	C1	11.3	7.6	8.5	11.6	17.7	8.1	>5.9
35FA+10Slag+15WS(C1)	C1	11.4	10.0	8.5	12.3	17.7	8.6	>8.0
35FA+10Slag+15WS(C1)	C1	11.6	8.1	8.6	12.4	17.7	8.5	>5.8
45CaSi+20WS(C2)	C2	11.3	7.6	8.5	11.6	17.0	8.1	>6.4
45CaSi+20WS(C2)	C2	11.4	7.6	8.6	11.7	17.0	7.9	>6.4
45CaSi+15WS(C2)	C2	11.3	7.6	8.6	11.6	17.0	8.0	>6.1
45CaSi+15WS(C2)	C2	11.4	7.7	8.7	11.8	17.0	7.9	>6.1
45FA+20WS(M)	M	10.6	8.1	8.5	12.3	17.0	8.9	>8.1
45FA+20WS(M)	M	10.6	8.1	8.5	12.3	15.0	9.0	>8.2
45FA+15WS(M)	M	10.7	8.1	8.5	12.3	16.7	8.7	>7.9
45FA+15WS(M)	M	10.6	8.1	8.5	12.3	16.8	8.7	>7.9
45CaSi+20WS(M)	M	11.0	7.7	8.5	11.5	17.4	8.2	>8.2
45CaSi+20WS(M)	M	11.1	7.7	8.5	11.5	17.3	8.1	>8.2
35FA+10Slag +15WS(M)	M	10.9	8.1	8.7	12.5	17.1	8.8	>7.9
35FA+10Slag+15WS(M)	M	10.9	8.1	8.6	12.4	17.1	8.9	>7.9

(a) Iodine was found below the detection level (<5 ppb). Detection level value was used to determine the LI.

Table 7.15. Weight Loss Results Determined in Water Immersion Tests for Ceramicrete Waste Forms Fabricated with WTP Secondary Waste Stream Simulants and Blank Samples (Singh et al. 2011)

Sample Composition	Waste Stream	Weight Loss (%-1 Month)	STDEV (1 Month)	Weight Loss (%-2 Month)	STDEV (2 Month)	Weight Loss (%-3 Month)	STDEV (3 Month)
45FA+20W	Baseline	8.93	0.48	9.63	0.59	10.10	0.35
45FA+15W	Baseline	8.27	0.68	9.50	0.35	9.22	0.92
45FA+10W	Baseline	7.61	0.43	9.02	0.28	8.56	0.67
45FA+5W	Baseline	6.98	0.19	8.74	0.46	8.70	0.59
45FABlank	Blank	7.39	0.13	8.05	0.90	7.83	0.86
45CaSi+20W	Baseline	10.00	0.02	11.87	0.08	12.27	0.07
45CaSi+15W	Baseline	11.08	0.077	11.94	0.24	12.27	0.07
45CaSiBlank	Blank	9.80	0.05	10.70	0.04	10.94	0.16
25CaSi+25W	Baseline	10.39	0.10	10.45	0.36	11.09	0.34
25CaSiBlank	Blank	8.43	0.13	8.89	0.25	9.20	0.46
25FA+25W	Baseline	12.86	0.44	12.51	1.10	12.18	1.14
25FABlank	Blank	11.69	0.39	13.11	0.14	13.24	0.54
25FA+25W+1B.Acid	Baseline	12.24	0.22	14.18	1.29	12.57	0.72
35FA+10Slg+10W	Baseline	6.26	0.70	6.81	0.42	7.35	0.86
35FA+10SlgBlank	Blank	6.29	0.13	7.38	0.71	7.23	0.80
35FA+10Slg+15W	Baseline	6.62	0.77	8.66	0.34	8.27	0.80
45FA+20W	Cluster 1	7.48	0.34	7.50	0.37	7.62	0.31
45FA+15W	Cluster 1	7.08	0.78	6.35	0.36	6.33	0.18
45FA+10W	Cluster 1	5.17	0.24	4.46	0.08	4.31	0.20
45FA+5W	Cluster 1	6.82	0.31	7.34	0.83	7.84	1.51
45FABlank	Blank	6.91	0.31	7.32	0.61	7.63	0.56
45CaSi+20W	Cluster 1	11.16	0.04	11.82	0.82	12.32	0.24
45CaSi+15W	Cluster 1	10.93	0.04	11.89	0.08	12.68	0.30
45CaSiBlank	Blank	10.18	0.07	11.38	0.12	12.11	0.58
25CaSi+25W	Cluster 1	11.35	0.48	12.29	0.39	12.50	0.51
25CaSiBlank	Blank	8.78	0.21	9.67	0.34	10.14	0.61

Table 7.15. (contd)

Sample Composition	Waste Stream	Weight Loss (%-1 Month)	STDEV (1 Month)	Weight Loss (%-2 Month)	STDEV (2 Month)	Weight Loss (%-3 Month)	STDEV (3 Month)
25FA+25W	Cluster 1	13.77	0.74	14.71	0.20	14.89	0.22
25FABlank	Blank	12.23	0.52	11.37	1.37	12.13	0.82
25FA+25W+1B.Acid	Cluster 1	14.30	0.49	15.32	0.79	15.06	0.24
35FA+10Slg+10W	Cluster 1	4.93	0.98	5.51	0.42	5.66	0.60
35FA+10SlgBlank	Blank	6.29	0.13	7.38	0.71	7.23	0.80
35FA+10Slg+15W	Cluster 1	6.12	0.20	7.31	0.44	6.81	0.09
45FA+20W	Cluster 2	9.81	0.61	8.70	0.18	8.47	0.82
45FA+15W	Cluster 2	8.87	0.34	7.82	0.33	8.02	0.08
45FA+10W	Cluster 2	9.02	1.84	9.06	0.30	8.20	1.35
45FA+5W	Cluster 2	8.85	1.79	7.32	0.66	6.56	1.02
45FABlank	Blank	7.39	0.13	8.05	0.59	7.83	0.86
45CaSi+20W	Cluster 2	11.97	0.06	12.04	0.16	12.59	0.13
45CaSi+15W	Cluster 2	11.83	0.86	12.00	0.38	12.67	0.05
45CaSiBlank	Blank	9.80	0.05	10.70	0.04	10.94	0.16
25CaSi+25W	Cluster 2	11.74	0.23	11.43	0.67	13.61	2.77
25CaSiBlank	Blank	8.43	0.13	8.89	0.08	9.20	0.46
25FA+25W	Cluster 2	11.62	1.82	14.94	5.96	13.44	0.84
25FABlank	Blank	11.69	0.39	13.11	0.08	13.24	0.54
25FA+25W+1B.Acid	Cluster 2	11.32	3.83	10.65	5.10	17.42	7.41
35FA+10Slg+10W	Cluster 2	5.99	1.33	6.89	0.35	5.78	0.93
35FA+10SlgBlank	Blank	6.29	0.13	7.38	0.71	7.23	0.80
35FA+10Slg+15W	Cluster 2	7.62	0.59	7.30	0.27	7.89	0.54
45FA+20W	Mixed	10.35	0.47	8.67	0.49	9.63	0.69
45FA+15W	Mixed	10.20	0.63	9.09	1.08	8.65	1.34
45FA+10W	Mixed	9.33	0.54	8.28	0.15	8.79	0.92
45FA+5W	Mixed	9.46	0.41	8.45	0.82	8.79	0.72

Table 7.15. (contd)

Sample Composition	Waste Stream	Weight Loss (%-1 Month)	STDEV (1 Month)	Weight Loss (%-2 Month)	STDEV (2 Month)	Weight Loss (%-3 Month)	STDEV (3 Month)
45FABlank	Blank	7.39	0.13	8.05	0.59	7.83	0.86
45CaSi+20W	Mixed	13.01	0.18	14.87	0.11	14.38	0.12
45CaSi+15W	Mixed	12.00	0.42	13.78	0.14	13.38	0.46
45CaSiBlank	Blank	9.80	0.05	10.70	0.04	10.94	0.16
25CaSi+25W	Mixed	12.55	1.30	14.27	1.24	12.21	1.33
25CaSiBlank	Blank	8.43	0.13	8.89	0.08	9.20	0.46
25FA+25W	Mixed	12.24	1.58	18.89	12.63	11.06	0.31
25FABlank	Blank	11.69	0.39	13.11	0.08	13.24	0.54
25FA+25W+1B.Acid	Mixed	20.67	1.63	17.13	4.34	20.80	0.24
35FA+10Slg+10W	Mixed	9.19	0.73	10.14	1.04	8.61	0.24
35FA+10SlgBlank	Blank	6.29	0.13	7.38	0.71	7.23	0.80
35FA+10Slg+15W	Mixed	10.00	1.27	10.33	0.84	10.89	0.45

8.0 Summary of Key Ceramicrete Attributes

Ceramicrete is a relatively new engineering material developed at Argonne National Laboratory to treat radioactive and hazardous waste streams (e.g., Wagh 2004; Wagh et al. 1999a, 2003; Singh et al. 2000). This cement-like waste form can be used to treat solids, liquids, and sludges by chemical immobilization, microencapsulation, and/or macroencapsulation. The Ceramicrete technology is based on chemical reactions between phosphate anions and metal cations to form a strong, dense, durable, and low porosity matrix that immobilizes hazardous and radioactive contaminants as insoluble phosphates and microencapsulates insoluble radioactive components. Ceramicrete is a type of phosphate-bonded ceramic, which are also known as CBPCs. The Ceramicrete binder is formed through an acid-base reaction between calcined magnesium oxide (MgO; a base) and potassium hydrogen phosphate (KH_2PO_4; an acid) in aqueous solution. The reaction product sets at room temperature to form a highly crystalline material. During the reaction, the hazardous and radioactive contaminants also react with KH_2PO_4 to form highly insoluble phosphates. Small amounts of additives are added to reduce Tc(VII) to less soluble Tc (IV) [$SnCl_2$ and Na_2S] and to precipitate radioiodine (silver zeolite). The salient characteristics and the results of performance testing of the Ceramicrete waste form are summarized below:

- **Waste Loading**
  Based on process demonstration testing (Singh et al. 2011), solid waste loading of ~1.2 wt.% and ~2.2 wt.% has been achieved using the Hanford secondary waste S1 and S4 simulants, respectively. The Na loading in both cases was equivalent to ~1 M.
- **The Critical Parameters for the Ceramicrete Process**
  1. There was degradation of the waste forms observed in the samples post ANS 16.1 tests. Fine cracks were observed in samples with fly ash and $CaSiO_3$ filler. Samples with fly ash + slag filler showed the most pronounced cracking. Several explanations were given as possible reasons for the occurance of this cracking. The first possible explanation was that swelling of the zeolite beads over time may have caused cracking. It was also indicated that unreacted MgO powder in the waste could hydrate to form $Mg(OH)_2$ during the ANS 16.1 or water immersion tests causing swelling and cracking. Another possibility indicated was that because the waste simulants are rich in Na a reaction between the zerolite and the pore fluid could form hydous amorphous sodium silicate resulting in expansion and cracking. In spite of the cracks, release of radionuclide surrogates did not increase indicating chemical binding of the species in the waste form was effective.
  2. Hydrogen generation resulting from radiolytic decomposition of water and organic compounds in Ceramicrete fabricated with secondary waste is not expected to be a significant issue.
  3. Preliminary scale-up of the process was conducted up to 2 gallons size waste forms. Use of minimal amounts of boric acid as a set retarder was used to control the mixing time to as much as 35 minutes.
  4. The Ceramicrete should set within a couple of hours and should be cured within 24 hours although heat dissipation may take longer depending on the size of the containers.
  5. Ceramicrete waste forms fabricated at the lowest fly ash concentration, using the mixed simulant (S4) at the highest waste concentration, and boric acid as a set retarder (sample composition

25FA+25W+1B.A), did not meet the minimum compressive strength requirement for IDF waste acceptance (3.54E6 Pa, 500psi).

- **Ceramicrete Flow Sheet**

  CH2M HILL developed a concept for a standalone facility for implementing the Ceramicrete process for Hanford secondary liquid wastes (Russell et al. 2006). As part of their Ceramicrete facility concept, an equipment list for the major equipment components was provided. The equipment is sized to process a maximum volume of 800,000 liters of 2M sodium secondary waste solution every 30 days with a 70 percent total operating efficiency. All vessels were sized to hold their contents at 85 percent capacity. Based on this conceptual design, the estimated cost for construction of the CTF for immobilizing HSW was estimated to be $48.5 million (in 2005 dollars).

- **Regulatory Leach Tests**

  TCLP (EPA Method 1311) results conducted on ceramicrete specimens fabricated with all waste simulants indicated that the concentrations of RCRA metals (Ag, As, Ba, Cd, Cr, Hg, Pb, and Se) in the leachates were well below the UTS 40 CFR 268.48 standards). ANSI/ANS 16.1 leach test results for Re (as a Tc surrogate) and I met the required standards. LI values calculated for Re ranged from 7.9 to 9.0, with no specific trend found with waste simulant or filler type. Iodine was below the detection limit in all leachates. Using the detection limit of 5 ppb, the worst-case LI values for I ranged from >5.8 to >8.2.

- **Compressive Strength**

  The only Ceramicrete waste form composition that did not meet the minimum compressive strength requirement for IDF waste acceptance (3.54E6 Pa, 500psi) was 25FA+25W+1B.A (mixed simulant).

9.0 References

ANS. 1986. "American National Standard Measurement of the Leachability in Solidified Low-Level Radioactive Wastes by a Short-Term Test Procedure, Method ANSI/ANS 16.1-1986." American Nuclear Society, La Grange Park, Illinois.

ASTM. 1997. "Standard Test Methods for Determining Chemical Durability of Nuclear, Hazardous, and Mixed Waste Glasses: The Product Consistency Test (PCT), ASTM C 1285-97." American Society for Testing and Materials, West Conshohocken, Pennsylvania.

Brinker CJ and GW Scherer. 1989. Chapters 1 and 4. In *Sol-Gel Science*, Academic Press, San Diego, California.

Brown WE and LC Chow. 1986. "A New Calcium Phosphate, Water-Setting Cement." In *Cements Research Progress*, PW Brown, ed, Westerville, Ohio, American Ceramic Society, pp. 352–379.

Buj I, J Torras, D Casellas, M Rovira, and J Pablo. 2009. "Effect of Heavy Metals and Water Content on the Strength of Magnesium Phosphate Cements." *Journal of Hazardous Materials* 170:345–350.

Buj I, J Torras, M Rovira, and J Pablo. 2010. "Leaching Behaviour of Magnesium Phosphate Cements Containing High Quantities of Heavy Metals." *Journal of Hazardous Materials* 175:789–794.

DOE Order 435.1. 1999. "Radioactive Waste Management." U.S. Department of Energy, Washington, D.C.

EPA. 1992. "Method 1311: Toxicity Characteristic Leaching Procedure." In *Response, Office of Solid Waste and Emergency, Test Methods for Evaluating Solid Waste, SW-846*. U.S. Environmental Protection Agency, Washington, D.C.

EPA. 1995. *Guidelines for Classification and Packing Group Assignment of Division 5.1, Materials.* CFR CH1 (10-1-95 Ed.), Appendix F to Part 173, U.S. Environmental Protection Agency, Washington, D.C.

Eubank WR. 1951. "Calcination Studies of Magnesium Oxide." *Journal of the American Ceramic Society* 34(8):225–229.

Fluor Hanford. 2005. *Conceptual Design Report for Effluent Treatment Facility Solidification Treatment Unit*. HNF-26914, Fluor Hanford, Richland, Washington.

Hunter J. 1981. *Zero Potential in Colloid Science.* Academic Press, New York.

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

NRC. 1991. *Technical Position on Waste Form*. U.S. Nuclear Regulatory Commission, Washington, D.C.

Pierce EM, SV Mattigod, RJ Serne, JP Icenhower, RD Scheele, W Um, N Qafoku, and JH Westsik, Jr. 2010a. *Review of Potential Candidate Stabilization Technologies for Liquid and Solid Secondary Waste Streams*. PNNL-19122, Pacific Northwest National Laboratory, Richland, Washington.

Pierce EM, W Um, KJ Cantrell, MM Valenta, JH Westsik, Jr., RJ Serne, KE Parker. 2010b. *Secondary Waste Form Screening Test Results – Cast Stone and Alkali Alumino-Silicate Geopolymer*. PNNL-19505, Pacific Northwest National Laboratory, Richland, Washington.

Pourbaix M. 1974. *Atlas of Electrochemical Equilibria in Aqueous Solutions.* Pergamon Press, New York.

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

Resource Conservation and Recovery Act of 1976. 1976. Public Law 94-580, as amended, 42 USC 6901 et seq. and 42 USC 6927(c) et seq.

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

Russell RL, MJ Schweiger, JH Westisk, Jr., PR Hrma, DE Smith, AB Gallegos, MR Telander, and SG Pitman. 2006. *Low Temperature Waste Immobilization Testing.* PNNL-16052, Rev. 1, Pacific Northwest National Laboratory, Richland, Washington.

Sakar AK. 1991. "Hydration/Dehydration Characteristics of Struvite and Dittmarite Pertaining to Magnesium Ammonium Phosphate Cement System." *Journal of Materials Science* 26:2314–2318.

Schwinkendorf WE and CE Cooley. 1999. "Cost of Mixed Low-Level Waste Stabilization Options." Proceeding of *Waste Management 1998*, Tucson, Arizona.

Singh D, AS Wagh, JC Cunnane, and JL Mayberry. 1997. "Chemically Bonded Phosphate Ceramics for Low-Level Mixed-Waste Stabilization." *Journal of Environmental Science and Health* A32(2): 27–541.

Singh D, AS Wagh, M Tlustochowicz, and SY Jeong. 1998. "Phosphate Ceramic Process for Macroencapsulation and Stabilization of Low-Level Debris Wastes." *Waste Management* 18:135–143.

Singh D, SY Jeong, K Dwyer and T Abesadze. 2000. "Ceramicrete: A Novel Ceramic Packaging System for Spent-Fuel Transport and Storage." Proceedings of *Waste Management 2K Conference*, Tucson, Arizona, February 27–March 2, 2000.

Singh D, VR Mandalika, SJ Parulekar, and AS Wagh. 2006. "Magnesium Potassium Phosphate Ceramic for ^{99}Tc Immobilization." *Journal of Nuclear Materials* 348:272–282.

Singh D, R Ganga, J Gaviria, and Y Ysufoglu. 2011. *Secondary Waste Form Testing Ceramicrete Phosphate Bonded Ceramics*. ANL-11/16, Argonne National Laboratory, Argonne, Illinois.

Sivaprasad P, K Ramesh, and YP Reddy. 1990. "Optical Absorption Spectrum of Nickel Doped $MgKPO_4 \cdot 6H_2O$." *Solid State Communications* 73(3):239–241.

Spence RD and C Shi. 2005. *Stabilization and Solidification of Radioactive and Mixed Waste*. CRC Press, Boca Raton, Florida.

Taylor AW, AW Frazier, and EL Gurney. 1963. "Solubility Products of Magnesium Ammonium and Magnesium Potassium Phosphates." *Transactions of the Faraday Society* 59:1580–1589.

THOR Treatment Technologies. 2009. *Report for Treating Hanford LAW and WTP SW Simulants: Pilot Plant Mineralizing Flowsheet.*, RT-21-002, Rev 1, THOR Treatment Technologies, LLC, Denver, Colorado.

U.S. Department of Energy, Office of River Protection (DOE-ORP). 2010. *River Protection Project System Plan*. ORP-11242, Revision 5, U.S. Department of Energy, Office of River Protection, Richland, Washington.

U.S. Department of Energy, Office of River Protection (DOE-ORP). 2011. *Justification of Mission Need for the Secondary Liquid Waste Treatment Project*. U.S. Department of Energy, Office of River Protection, Richland, Washington.

Vinokurov SE, YM Kulyako, OM Slyuntchex, SI Rovny, and BF Myasoedov. 2009. "Low-Temperature Immobilization of Actinides and Other Components of High-Level Waste in Magnesium Potassium Phosphate Matrices." *Journal of Nuclear Materials* 385:189–192.

Wagh AS. 2004. *Chemically Bonded Phosphate Ceramics*. Elsevier, New York.

Wagh AS and SY Jeong. 2003. "Chemically Bonded Phosphate Ceramics: I, A Dissolution Model of Formation." *Journal of the American Ceramic Society* 86(11):1838–1844.

Wagh AS, SY Jeong, D Singh, RV Strain, H No, and J Wescott. 1997. "Stabilization of Contaminated Soil and Wastewater with Chemically Bonded Phosphate Ceramics." ANL/ET/CP-91063, Proceedings of *Waste Management 1997 Conference*, March 2-7, 1997, Tucson, Arizona.

Wagh AS, SY Jeong, and D Singh. 1999a. "High Strength Phosphate Cement Using Industrial Byproduct Ashes." Proceedings of *the 1st International Engineering Foundation Conference on High Strength Concrete*, July 13-18, 1997, Kona, Hawaii.

Wagh AS, D, R Strain, SY Jeong, D Reed, T Krause and D Singh. 1999b. "Stabilization of Rocky Flats Pu-Contaminated Ash within Chemically Bonded Phosphate Ceramics." *Journal of Nuclear Materials* 265:295–307.

Wagh A, D Singh, and SY Jeong. 2001. "Chemically Bonded Phosphate Ceramics for Stabilization and Solidification of Mixed Waste." *Encyclopedia of Environmental Technology*, CRC Press, pp. 6.3-1 to 6.3-18.

Wagh AS, MD Maloney, GH Thomson, and A Antink. 2003. "Investigations in Ceramicrete Stabilization of Hanford Tank Wastes." Proceedings of *Waste Management 2003 Conference*, eds R Post and M Wacks, February 23–27, 2003, Tucson, Arizona.

Washington State Department of Ecology, U.S. Environmental Protection Agency and U.S. Department of Energy (Ecology, EPA, and DOE). 1989. *Hanford Facility Agreement and Consent Order, As Amended*. Washington State Department of Ecology, U.S. Environmental Protection Agency, and U.S. Department of Energy, Olympia, Washington.

Appendix A

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

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
Maximize operability	Operability risk	Independent expert assessment to include number of unit operations, equipment count, etc.	Process description, flowsheet description

Supplemental Treatment Technology Selection Decision Goals, Criteria, and Measures(a)

Goal	Criterion	Measures	Data Package Contents
Minimize overall system interface impacts	System interface impacts	Liquid effluent greater that Effluent Treatment Facility (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, TM Brouns. 2004. *Initial Selection of Supplemental Treatment Technologies for Hanford's Low-Activity Tank Waste*. RPP-19763, WM-04 Conference, February 29-March 4, 2004, Tucson, Arizona.

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/ANS16.1, EPA 1315, ASTM 1308. Location of contaminants within waste form phases, mechanisms of containment, mechanisms of release, dissolution of waste form phases, diffusion coefficients/LI 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 3× (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/ANS16.1, EPA 1315, ASTM 1308. Location of contaminants within waste form phases, mechanisms of containment, mechanisms of release, dissolution of waste form phases, diffusion coefficients/LI 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 3× (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.

Summary of Testing Recommendations for Containerized Grout Technology—Waste Form Performance(a)

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 a loading suggested by the 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.	Do not expect to see any data on actual secondary wastes. Look at work done with actual LAW wastes.
		At a loading suggested by the vendor, produce a fourth waste form sample from simulated waste and another from actual waste. Conduct TCLP tests on a sample from the simulant and a sample from actual waste cured under identical conditions.	
	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 verify that regional differences in solidification agents will not introduce potential consistency problems.	Identify and describe any work looking at alternative sources of dry materials.

Summary of Testing Recommendations for Containerized Grout Technology—Waste Form Performance(a)

Technical Issue/Uncertainty	Testing Objective	Specific Testing	Data Package Content
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
	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 released during the 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, 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 (ETF) 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 a draft 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 WAC. The fifth column identifies the data package content to address the requirement.

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 use one of the currently planned disposal system packages and corresponding interfaces. The use of a different container may be more efficient, but will have to be evaluated against the disposal system impacts.	4.3.1 Package Construction Containers must be made of or lined with materials that will not react with, and are otherwise compatible with, the dangerous waste during handling and storage before disposal such that the capability 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.

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
1.2.2.3 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	4.3.2 Size 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 x 1.2 m high x 2.4 m long (4-ft x 4-ft x 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 it is assumed that they were fully loaded with supplemental ILAW glass.		Waste load and density

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
1.2.2.5 Closure and Sealing	A means of mitigating hydrogen generation shall be provided in the package closure design. A Nucfil 013™ filter (or equivalent) shall be used in combination with a hydrogen recombination catalyst to prevent loss of radionuclides from the container or hydrogen accumulation in the disposal configuration. Pouring a non-radioactive cold cap as a filler material is recommended.	Provide equivalence to HNF-EP-0063, Rev 10, Section 3.36, Gas Generation. Some level of radiolytic decomposition may occur in the SSW and hydrogen may evolve.	4.1.11 Gas Generation When waste is packaged, vents or other measures shall be provided if the potential exists for pressurizing or generating flammable or explosive concentrations of gases within the waste container.	Package closure and sealing not expected to be a factor in waste form selection.
1.2.2.6 Labeling	Each package shall be labeled in accordance with the requirements of the Integrated Disposal Facility Waste Acceptance Criteria. (RPP-8402)	See 1.2.2.2 Package Description	4.3.5 Marking and Labeling Containers of low-level waste 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 10 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 (12); i.e., the container shall be at least 90 percent full when placed in the landfill.	4.1.4 Solidification and Stabilization All containerized waste must fill at least 90 percent of the internal volume of the container when placed in the disposal unit.	Describe process demonstrations, bench, engineering, pilot, and full-scale.

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
1.2.2.8 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 10CFR61.55 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 exceed 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

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
1.2.2.9 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 49CFR172.101 (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	<u>4.2.1 Radiological Concentration</u> 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 milliSieverts 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	<u>4.2.6 Dose Rate Limits</u> Containers with dose rates less than or equal to 2 milliSieverts 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 49CFR173.443(a).	Interface with the disposal system	<u>4.2.4 Package Removable Contamination</u> 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

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

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
1.2.2.13 Free Liquids	The package shall contain no detectable free liquids as defined in ANSI/ANS-55.1 or SW-846 Method 9095.	Compliance with 10CFR61	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 verify 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.

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
1.2.2.14 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.	4.1.9 Explosives 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. 4.1.10 Pyrophoric Wastes 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.	4.1.11 Gas Generation 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.

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
1.2.2.16 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 CFR268. 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 verify that limits for regulated metals are met.	Compliance with applicable Washington State and federal RCRA requirements.	<u>4.1.1 Hazardous Waste</u> 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. <u>4.1.2 Land Disposal Restrictions</u> All waste subject to Resource Conservation and Recovery Act of 1976 LDR) (40 CFR 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.

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
1.2.2.17 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 49CFR173.465(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.

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
1.2.2.19 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 268).	Not a factor in waste form selection.

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
1.2.2.20 Waste Form Testing - Leachability Index	The waste form shall have a sodium LI greater than 6.0 when tested for 90 days in deionized water using the ANSI/ANS-16.1 procedure. In addition, LI performance targets have been established for key radionuclides of concern—iodine and technetium. An iodine-129 LI greater than 11.0 and a technetium-99 LI greater than 9.0 are desired.	10CFR61 and NRC Waste Form Technical Position. Performance targets were established based on preliminary risk and PA 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: the ANSI/ANS 16.1 procedure and corresponding leachability indices are 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 DIW 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.

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
1.2.2.22 Thermal, Radiation, Biodegradation and Immersion Stability	The ILAW product shall be resistant to thermal, radiation, biodegradation, and immersion degradation, as described in NRC *Technical Position on Waste Form*. Resistance to each of these types of degradation shall be established by showing that the mean compressive strength of representative non-radioactive samples shall be equal to or greater than 3.45E06 Pa and not less than 75 percent of the initial compressive strength after subjecting the samples to the following: Thermal Degradation: Thirty thermal cycles between a high of 60°C and a low of -40°C in accordance with the ASTM B553-79 or an equivalent testing method. Radiation Degradation: Exposure to a minimum radiation dose of 1.0E08 rad or to a dose equivalent to the maximum level of exposure expected from self-irradiation during storage, transportation and disposal if this is greater than 1.0E08 rad. 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.	Compliance with 10CFR61 and NRC Waste Form Technical Position.	4.2.1 Radiological Concentration Category 3 waste can be disposed of only if the waste meets one of the following conditions of waste form stability. Stabilization in concrete or other stabilization agents. The stabilized waste must meet the LI 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.

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
1.2.3 Package Handling	The package shall be compatible with crane lifting and movement. The package shall be equipped with lifting and other handling appurtenances designed to allow safe lifting, movement, and stacking of the packages when fully loaded. The package shall maintain its integrity during handling, transportation, and stacking. The package design shall allow for vertical stacking to a total height of 10 meters.	Interface with current disposal system	<u>4.3.4 Handling</u> All packages must be configured for safe unloading by forklift or crane. Packages that must be unloaded by crane shall be equipped with lifting and other appurtenances designed to allow safe lifting, movement, and stacking of the packages when fully loaded. The package shall maintain its integrity during handling, transportation, and the lifting required for disposal in IDF.	Package design. Not expected to impact waste form selection.

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

Distribution

No. of
Copies

OFFSITE

1 D Singh
Argonne National Laboratory
9700 South Case Avenue
Argonne, IL 60439

No. of
Copies

ONSITE

4 Washington River Protection Solutions

MA Melvin	E6-30
DJ Swanberg	B1-55
KE Smith	E6-30
LE Thompson	E6-20

11 Pacific Northwest National Laboratory

PR Bredt	K9-09
KJ Cantrell	K6-81
CW Chung	K6-24
GB Josephson	K9-69
MJ Lindberg	P7-54
SV Mattigod	K3-62
LM Peurrung	K9-09
N Qafoku	P7-54
RJ Serne	K6-81
W Um	P7-54
JH Westsik, Jr	K7-15

Pacific Northwest
NATIONAL LABORATORY

Proudly Operated by Battelle *Since 1965*

U.S. DEPARTMENT OF
ENERGY

902 Battelle Boulevard
P.O. Box 999
Richland, WA 99352
1-888-375-PNNL (7665)
www.pnl.gov