1 OF 2

*Technical Area
Status Report
for
Low-Level Mixed Waste
Final Waste Forms*

Volume 1

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**TECHNICAL AREA STATUS REPORT
FOR
LOW-LEVEL MIXED WASTE
FINAL WASTE FORMS**

Volume I

August 1993

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ACRONYMS AND ABBREVIATIONS

AEC	Atomic Energy Commission
ALT	Accelerated Leaching Test
ANC	Acid Neutralization Capacity
ANS	American Nuclear Society
ANSI	American National Standards Institute
ASTM	American Society for Testing and Materials
AVM	Ateliers de Vitrification de Marcoule
BDAT	Best Demonstrated Available Technology
BNL	Brookhaven National Laboratory
BWR	Boiling Water Reactor
CFR	Code of Federal Regulations
CIF	Consolidated Incineration Facility
DLT	Dynamic Leach Test
DOE	U.S. Department of Energy
DOT	U.S. Department of Transportation
DWPF	Defense Waste Processing Facility
EDTA	Ethylene Diamine Tetraacetic Acid
ELT	Equilibrium Leach Test
EP	Extraction Procedure
EPA	U.S. Environmental Protection Agency
ERDA	U.S. Energy Research and Development Administration
FWF	Final Waste Form
HEPA	High Efficiency Particulate Air
IAEA	International Atomic Energy Agency
IFR	Integral Fast Reactor
INEL	Idaho National Engineering Laboratory
ISV	In Situ Vitrification
LANL	Los Alamos National Laboratory
LDPE	Low Density Polyethylene
LDR	Land Disposal Restriction
LI	Leachability Index
LLNL	Lawrence Livermore National Laboratory
LLMW	Low-Level Mixed Waste
LLW	Low-Level Radioactive Waste
LOMI	Low Oxidation-state Metal Ion
MCC-1-P	Materials Characterization Center Static Leach Test
MEP	Methyl Ethyl Pyridine
MEP	Multiple Extraction Procedure
MRS	Monitored Retrievable Storage
MW	Mixed Waste
MWEP	Monofill Waste Extraction Procedure
MWIP	Mixed Waste Integrated Program

MWTP	Mixed Waste Treatment Project
NDT	Non-Destructive Test
NRC	U.S. Nuclear Regulatory Commission
NTA	Nitrilotriacetic Acid
ORNL	Oak Ridge National Laboratory
OSU	Oregon State University
PA	Performance Assessment
PCB	Polychlorinated Biphenyl
PCC	Portland Cement Concrete
PCT	Product Consistency Test
PNL	Pacific Northwest Laboratory
PWR	Pressurized Water Reactor
QA/QC	quality assurance/quality control
R&D	Research and Development
RCRA	Resource Conservation and Recovery Act
RFP	Rocky Flats Plant
RREL	Risk Reduction Engineering Laboratory
SCE	Sequential Chemical Extraction
SEG	Scientific Ecology Group
SPC	Sulfur Polymer Cement
SRS	Savannah River Site
TASR	Technical Area Status Report
TCLP	Toxicity Characteristic Leaching Procedure
TRU	Transuranic
TSG	Technical Support Group
TTP	Technical Task Plan
UF	Urea Formaldehyde
WERF	Waste Experimental Reduction Facility
WHC	Westinghouse Hanford Company
WS	Waste Stream

NOMENCLATURE

Ag	silver
AgCl	silver chloride
AgF	silver fluoride
AgI	silver iodide
Al	aluminum
Al ₂ O ₃	aluminum oxide
Al ₂ O ₃ -SiO ₂	aluminosilicate
AlPO ₄	berlinite (aluminum phosphate)
As	arsenic
AsI ₃	arsenic iodide
As ₂ O ₃	arsenic trioxide
B	boron
Ba	barium
BaCl ₂	barium chloride
BaO	barium oxide
BaF ₂	barium fluoride
Be	beryllium
B ₂ O ₃	boron oxide
B ₂ O ₃ -SiO ₂	borosilicate
BTU	British Thermal Units
BTU/h ft °F	BUTs/hour-foot-degrees Fahrenheit (thermal conductivity)
°C	degrees celsius
C	carbon
Ca	calcium
CaO	calcium oxide (lime)
CaO-Al ₂ O ₃ -SiO ₂ -H ₂ O	anorthite
Cd	cadmium
CdBr ₂	cadmium dibromide
CdF ₂	cadmium fluoride
CdI ₂	cadmium iodide
CdO	cadmium oxide
CH ₄	methane
Cl	chlorine
cm	centimeters
Cm	curium
cm/d	centimeters per day
Co	cobalt
CO ₂	carbon dioxide
cP	centipoise
Cr	chromium
CrO ₃	chromium trioxide

CrF_3	chromium fluoride
CrCl_3	chromium chloride
Cs	cesium
Cu	copper
$^{\circ}\text{F}$	degrees Fahrenheit
F	fluorine
Fe	iron
Fe_2O_3	ferric oxide (hematite)
ft	feet
g	grams
g/cm^3	grams per cubic centimeter
h	hour
H	hydrogen
H_3AsO_3	arsenious acid
H_2S	hydrogen sulfide
Hg	mercury
HgBr_2	mercury bromide
HgCl_2	mercury chloride
HgF_2	mercury fluoride
HgI_2	mercury iodide
hr	hour
in.	inches
K	Kelvins
K	potassium
KCl	potassium chloride
kg	kilograms
kg/day	kilograms per day
l	liters
lb	pounds
l/day	liters per day
Li	lithium
LiCl	lithium chloride
m	meters
m^3	cubic meters
Mg	magnesium
MgF_2	magnesium flouride
$\text{Mg}(\text{NH}_4)\text{PO}_4$	magnesium ammonium phosphate
MGy	millions of gray (1 gray = 100 rads)
min	minutes
Mn	manganese
Mo	molybdenum
MPa	mega-pascal
Na	sodium
$\text{NaAl}(\text{OH})_4$	sodium-aluminum hydroxide

NaCl	sodium chloride
NaNO ₂	sodium nitrite
NaNO ₃	sodium nitrate
Na ₂ O	sodium oxide
Na ₂ O-CaO-SiO ₂	sodalime silica glass
NaOH	sodium hydroxide
Na ₂ SO ₄	sodium sulfate
Ni	nickel
NO _x	oxides of nitrogen
O	oxygen
P	phosphorus
P ₂ O ₅	diphosphorus pentoxide
Pb	lead
PbBr ₂	lead bromide
PbCl ₂	lead chloride
PbF ₂	lead fluoride
PbI ₂	lead iodide
PbO	lead oxide
Pd	palladium
psi	pounds per square inch
Pu	plutonium
Rh	rhodium
Ru	ruthenium
S	sulfur
Se	selenium
SeOCl ₂	selenium oxychloride
SeOF ₂	se'enium oxyfluoride
Si	sil con
SiO ₂	silica
SO _x	oxides of sulfur
Sr	strontium
Tc	technetium
Ti	titanium
TiO ₂	titanium dioxide
U	uranium
vol%	volume percent
W/m-K	thermal conductivity (watts/meter-Kelvin)
wt%	weight percent
Zn	zinc
Zr	zirconium
ZrPO ₄	zirconium phosphate

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1. INTRODUCTION

The Office of Environmental Restoration and Waste Management (EM) was established by the Department of Energy (DOE) to direct and coordinate waste management and site remediation programs and activities throughout the DOE complex. To successfully achieve the goal of properly managing waste and the clean-up of the DOE sites, EM was divided into five organizations: the Office of Planning and Resource Management (EM-10); the Office of Environmental Quality Assurance and Resource Management (EM-20); the Office of Waste Operations (EM-30); the Office of Environmental Restoration (EM-40); and the Office of Technology Development (EM-50).

The mission of the Office of Technology Development (OTD) is to develop treatment technologies for the operational and environmental restoration wastes where current treatment technologies are inadequate or not available. The Mixed Waste Integrated Program (MWIP) was created by OTD to assist in the development of treatment technologies for the DOE low-level mixed wastes (LLMW). Currently, much of the DOE's large inventory of LLMW is out of compliance with the Land Disposal Restrictions (LDRs) promulgated by the Environmental Protection Agency (EPA), making treatment of these wastes an important issue.

The waste streams considered by MWIP are the DOE LLMWs which were identified by the EM-30 Mixed Waste Treatment Project (MWTP). The MWTP divided the waste streams into seven general categories: aqueous liquids, organic liquids, inorganic solids, metal wastes, organic solids, heterogeneous wastes, and special wastes. A brief summary of the description of these waste categories is presented below. Further descriptions of each waste category and subcategory are provided in Appendix A.

- **Aqueous Liquids** Aqueous liquids contain less than 1% organic content, and are pumpable. This category includes corrosive acids, corrosive bases, reactive cyanides, and toxic metals. Contaminants include mercury, lead, and trace amounts of other toxic metals and hazardous organics.
- **Organic Liquids** Organic liquids include more than 1% organic content and most, but not all, streams are pumpable. This category includes non-halogenated organics, halogenated organics, and scintillation cocktails. Other contaminants include mercury and trace amounts of other toxic metals.
- **Inorganic Solids** Inorganic solids contain wet solids and dry solids. The wet inorganic solids are non-pumpable and includes sludges, filter cakes, residues, absorbed liquid in vermiculite or clay, ion exchange resins, and salt cakes. Dry inorganic solids include processing salts, grouted or cemented sludges, ash, dust, soil, glass, ceramic crucibles, and brick.

- **Metal Wastes** Metal wastes include mixed ferrous and nonferrous metal pieces of various sizes and shapes. This category also includes liquid mercury, lead in the forms of bricks, shipping casks, or shielding materials, and activated lead. Contaminants include trace amounts of other toxic metals.
- **Organic Solids** Organic solids include wet organics, paints and paint residues, resins, animal carcasses, wood, plastic, rubber, paper, cloth, rags, heavy sludges, asphalt, graphite, and carbon.
- **Heterogeneous** Heterogeneous wastes include mixtures of organic, inorganic, and metallic wastes. This category includes construction, cleanup and process debris, lab packs, gloveboxes, HEPA filters, reactor equipment, glovebox gloves, shielding aprons, lead acid batteries, and mercury-contaminated materials. Heterogeneous wastes also include trace amounts of other toxic metals.
- **Special Waste** Special waste includes waste streams that require extra care for treatment. This category includes tritium wastes, pyrophorics, nitrated rags and filters, compressed gases, beryllium waste, and polychlorinated biphenyl (PCB) solids and liquids.

The MWIP is developing a unified approach for the treatment of all DOE LLMW presently in the inventory and that which is being generated. Only a small percentage of DOE's LLMW can be treated by available treatment facilities. The development of technologies for a "complete waste treatment system" capable of effectively treating all of the various types of DOE wastes is the ultimate goal of the MWIP. The MWIP will assist Waste Operations (EM-30) and Environmental Restoration (EM-40) in applying these technologies on a full-scale level, providing technical support throughout the design, construction, startup, and operation of the treatment systems. The end result of this work will be to develop and demonstrate technologies that are safe and cost effective, and are able to adequately treat the DOE LLMW to meet all appropriate requirements.

The MWIP has established five Technical Support Groups (TSGs) which provide assistance in identifying and developing treatment technologies: (1) Front-End Waste Handling; (2) Physical/Chemical Treatment; (3) Waste Destruction and Stabilization; (4) Second-Stage Destruction and Offgas Treatment; and (5) Final Waste Forms. Each TSG has assembled experts in the pertinent areas covered by the particular TSG. These experts are from the DOE sites, DOE contractors, EPA, and NRC. Each TSG has several vital functions that are integral steps in developing a unified solution to the waste management problems of the DOE complex.

The FWF Technical Area Status Report (TASR) Working Group, the Vitrification Working Group, and the Performance Standards Working Group were established as subgroups to the FWF TSG. The FWF TASR WG is comprised of technical representatives from most of the major DOE sites, the Nuclear Regulatory Commission (NRC), the EPA Office of Solid Waste, and the EPA's Risk Reduction Engineering Laboratory (RREL). The primary activity of the FWF TASR Working Group was to investigate and report on the current status of FWFs for LLMW in this TASR.

The FWF TASR Working Group determined the current status of the development of various waste forms described above by reviewing selected articles and technical reports, summarizing data, and establishing an initial set of FWF characteristics to be used in evaluating candidate FWFs; these characteristics are summarized in Section 2. After an initial review of available information, the FWF TASR Working Group chose to study the following groups of final waste forms: hydraulic cement, sulfur polymer cement, glass, ceramic, and organic binders. The organic binders included polyethylene, bitumen, vinyl ester styrene, epoxy, and urea formaldehyde. Section 3 provides a description of each final waste form. Based on the literature review, the gaps and deficiencies in information were summarized, and conclusions and recommendations were established.

The information and data presented in this TASR are intended to assist the FWF Production and Assessment TSG in evaluating the Technical Task Plans (TTPs) submitted to DOE EM-50, and thus provide DOE with the necessary information for their FWF decision-making process. This FWF TASR will also assist the DOE and the MWIP in establishing the most acceptable final waste forms for the various LLMW streams stored at DOE facilities.

2. TECHNICAL AREA CRITERIA

Treatment and disposal of mixed waste are being planned for the purpose of protecting human health and the environment from risks associated with the release of hazardous and radioactive components from the LLMW. DOE Order 5820.2A requires a Performance Assessment (PA) for each disposal site. The PA is intended to show by analysis that the waste treatment process, the processed waste form, and other disposal controls adequately meet this objective. At present, the site-specific PAs do not credit the waste form with any capacity to restrict contaminant mobility; all containment is attributed to physical barriers such as vaults. In order to rate the waste form as a physicochemical barrier to contaminant release, performance criteria must be developed. Criteria can be based solely on regulatory requirements, solely on material properties, or on a mixture of both. The last approach was selected, recognizing that current regulatory criteria do not address all of the properties of a waste form that determine its ability to reduce contaminant mobility in relation to time, and that the properties specified by the current regulatory criteria may not, in fact, be indicative of the performance of a particular waste form in its specific disposal setting.

Any methods used to treat or dispose of mixed wastes must adhere, as a minimum, to the relevant provisions of the Resource Conservation and Recovery Act (RCRA) and the Atomic Energy Act. A particular mixed waste may be either a characteristic hazardous waste or a listed hazardous waste. If the waste is characteristically hazardous, it must be treated to eliminate the characteristic prior to disposal in a non-hazardous waste landfill. The characteristic hazards are ignitability, corrosivity, reactivity, and toxicity. A waste is described as having the toxicity characteristic if the waste leaches more than specified amounts of organic or inorganic constituents when subjected to a specific leaching procedure. If the waste is hazardous because it is a listed hazardous waste, it must be disposed of in a hazardous waste landfill. In addition, if the waste falls under the Land Disposal Restrictions ("landban"), it must be treated to a certain level or by a specified technology before it can be disposed of in the hazardous waste landfill. Listed wastes can be "delisted" for a particular facility if a petitioner can provide compelling evidence showing that the particular waste (raw or treated) does not pose the hazard for which the waste type was originally listed. For the purposes of this document, it was assumed that DOE would not immediately pursue the delisting option and, therefore, that the waste form performance criteria would have to include compliance with the regulatory criteria for characteristic, listed, and landbanned wastes.

There is no specific set of regulations that addresses the radioactive component of DOE's LLMW. NRC has issued regulations and guidance for criteria for the disposal of low level radioactive waste, but DOE is not required to follow the NRC requirements. For the purposes of this document, it has been assumed that it would be to DOE's advantage to use these criteria to facilitate acceptance by the EPA and the respective state regulatory authorities. The Savannah River Site (SRS) and the Idaho National Engineering Laboratory (INEL) are already adopting this position for both low-level and mixed wastes.

In addition to the criteria based on regulatory requirements and guidance, we have defined other desirable characteristics of waste forms. Most important is the long term durability of the waste form in the disposal setting. This information is critical in developing the performance assessment, which documents the ability of the entire waste control system to prevent unacceptable releases. Compositional flexibility, minimal volume increase, and low unit cost are all desirable properties of final waste forms because of the large volume and wide heterogeneity of LLMW. Compositional flexibility will allow the application of a single demonstrated formulation or treatment to a wider variety of wastes.

Tests to measure and predict release rates of hazardous and radioactive constituents of mixed wastes over either the short- or the long-term have not been universally accepted or verified.

2.1 FINAL WASTE FORM CHARACTERISTICS

The task of determining pertinent characteristics of final waste forms was initiated by first recognizing the needs to protect the environment and to meet regulatory requirements for disposal, as described above; however, current EPA requirements for the hazardous component and NRC requirements for the radioactive component of a LLMW do not provide sufficient information to perform a risk-based analysis for a specific disposal site (DOE Order 5820.2A). Therefore, the pertinent waste form characteristics chosen for this TASR include additional ones that generate information required to conduct a performance assessment.

Table 1.1 lists the waste form characteristics which were chosen for consideration in this report. These characteristics provide an assessment of the ability of the final waste form to meet long-term performance, stability, and regulatory requirements. This table of characteristics was generated from an initial list of characteristics that is documented in Appendix B.

Table 1.1 includes the waste characteristics identified in the NRC guidelines for LLW forms (compressive strength, thermal cycling, radiation and biological stability, leach resistance, immersion resistance, and free liquid). These characteristics will help to ensure the structural stability of the final waste form as prescribed in 10 CFR 61.56. Guidelines for measuring these characteristics, as well as more detailed descriptions, have been published by the NRC¹ and are cited in Table 2.1. The leach resistance characteristic has been expanded to include both the hazardous and radioactive components of the waste. EPA and NRC have established different tests to assess the leachability of wastes and waste forms; therefore, determining the overall leach resistance of a waste form will either require more than one existing leach procedure, or the development of a new procedure covering both components. Because regulatory tests are designed to simulate a worst-case scenario or to provide a single value for comparing multiple waste forms, they often do not provide the rate-based or mechanistic data needed for modelling contaminant migration over the time periods simulated in a performance assessment.

Table 2.1. Pertinent final waste form characteristics

Characteristic	
Compressive Strength	Free Liquids
Thermal Stability	Chemical Durability
Radiation Stability	Gas Generation
Biological Stability	RCRA Compliance
Leach Resistance	Compositional Flexibility
Immersion Stability	----

In an attempt to evaluate the long-term isolation capability of the waste forms, the additional waste form characteristics shown in Table 2.1 were also included: chemical durability, gas generation, and compositional flexibility. Although quantitative methods for measuring these characteristics have not been established, they address the requirement for long-term stability. A short explanation of these waste form characteristics and the rationale for selecting each one follows:

Chemical Durability - This characteristic addresses the need to understand the chemical reactions that occur between the waste and binder, the waste form and the disposal container, and/or the waste form and the surrounding environment. Since the leach resistance characteristic was geared toward short-term performance (NRC and EPA tests), a more detailed understanding of the chemical behavior of the waste form is required to establish long-term performance and provide source terms for the performance assessment. Although a number of procedures for determining contaminant release over time were discussed, a consensus was not reached that any available method had been demonstrated to be accurate for this purpose. Procedures for determining this characteristic are identified as a technical need.

Gas Generation - This characteristic could also be included with Chemical Durability, Radiation Stability, or Biological Stability; however, it was felt that the gas generation characteristic was important enough to be addressed separately due to the potential safety issues associated with the storage and handling of waste forms that generate significant quantities of gas over a given period of time.

Compositional Flexibility - This characteristic is essential to identify a workable suite of final waste forms for application at DOE sites. The number of LLMW streams, and the variation and unknown nature of individual waste streams, may require

treatment formulations that will successfully stabilize contaminants as the concentration, mixture, and matrix change, without the additional requirements that detailed characterization be conducted on LLMW streams or that additives be constantly adjusted to make a successful FWF.

2.2 UNIFORM TESTS

Standard tests should be used to evaluate waste form characteristics so that test results for different waste forms will be comparable. The tests included in this section are those that measure (or purport to measure) the waste form characteristics selected in Section 2.1. Where possible, current EPA and NRC regulations/guidelines were used to select the tests listed in Table 2.1. However, it should be noted that standard tests may or may not be reflective of the real performance of the waste form in the disposal setting. These tests also may have limited applicability as source terms for the PA (DOE Order 5820.2A).

The goal of characterization is to demonstrate and quantify the effectiveness and long-term performance of the final waste form. This quantitative goal is necessary to demonstrate that the waste form satisfies the spirit of environmental protection laws as well as the letter of the regulations. A lesser role of the characterization tests is to compare the relative performance of different waste form types. Standard tests designed to measure the relevant waste form characteristics developed in Section 2.1 are listed in Table 2.1.

The most important characteristics of the waste form are its chemical and physical durability over time. While tests are available for most of the desired properties, the tests are generally of the 'index' type: acceptable/unacceptable [e.g., Toxicity Characteristic Leaching Procedure (TCLP), strength] or relative desirability (e.g., ANS 16.1-derived leachability indices). The tests are generally accepted as reasonable for comparing prospective formulations. However, none is proven to correlate with leaching (magnitude and rate) under field conditions.

The release of contaminants from the waste form over time determines the burden placed on the remainder of the waste containment system. Since the regulatory tests listed in Table 2.1 may not be suitable for this purpose, other leaching tests designed to simulate release rates and waste form aging are summarized in Table 2.2. Like the regulatory tests cited in Table 2.1, these tests need to be validated as accurate predictors of final waste form performance over the required life of the waste containment system.

2.3 STATUS OF PERFORMANCE CRITERIA

The foregoing sections describe characteristics of waste forms that are expected to contribute to their ability to physically and chemically contain the radioactive and hazardous constituents in mixed wastes. While the desirable characteristics are relatively easy to identify, the quantitative tests and numerical criteria used to measure short- and long-term performance of the waste forms are more problematic. Tests are available for assessing compliance with EPA's hazardous waste regulations and NRC's radioactive

Table 2.2. Properties, tests, and criteria for the characterization of final waste forms for mixed wastes established by regulatory agencies

PROPERTIES	APPLICABLE TESTS*	PERFORMANCE CRITERIA	ISSUES
Compression Strength	*ASTM C 39 (cement-based) ASTM D 1633 (soil cements) ASTM D 1074 (bitumen) Other tests	>0.41 MPa (60 psi) per NRC guidelines. Cement-bonded waste forms should have minimum compressive strength of 3.4 MPa (500 psi).	Is strength related to leachability or long-term durability? Is strength relevant for all forms?
Resistance to Thermal Cycling	*ASTM B 553 (freeze-thaw) ASTM D 4842 (freeze-thaw) ASTM C39	NRC requirement of 30 thermal cycles between 60°C (140°F) and -40°C (-40°F), and then still meet compressive strength criteria.	What temperature range is realistic? What minimum performance should be acceptable?
Radiation Stability	*10 ⁴ rad exposure; ASTM C 39	Should be exposed to minimum of 10E+06 Gy (10E+08 rad) in gamma irradiator, and then still meet compressive strength criteria.	No standard method. What total dose and dose rate are realistic for LLMW?
Chemical Durability	No standard method. BNL and University of Cincinnati are developing procedures	TBD	Interactions between waste, binder, container and disposal environment over the long-term.
Gas Generation	No standard method	TBD	---
Biological Stability	*ASTM G 21 & 22; ASTM C 39	TBD	What organisms should be used for specific disposal settings?
Leach Resistance	*ANS 16.1 **EPA 1311 (TCLP) Others (see Table 2.2)	ANS: LI>6.0; maintain compressive strength requirements. TCLP: meet concentration limit for listed or characteristic waste.	Diffusion vs. equilibrium. No verification that tests simulate field behavior, short- or long-term.
Free Liquids	*ANS 55.1 Appendix 2 **EPA 9095 (SW 846)	<0.5% vol. free liquids per NRC guidelines. Free liquid pH between 4 and 11; for cement-solidified waste, free liquid minimum pH of 9.	---
Hydraulic Parameters	Porosity, hydraulic conductivity, density, permeability	TBD	What data are required for modeling? Which test methods are appropriate?
RCRA Compliance	**EPA 1311 (TCLP) **40CFR261 tests for reactivity, corrosivity, and ignitability; compliance with land disposal restrictions.	Different criteria for characteristic, listed, and landbanned hazardous wastes.	May be difficult to identify correct waste code for mixed wastes; Best Demonstrated Available Technology (BDAT) may not be appropriate for radioactive waste.
Immersion	*ANS 16.1 (90-day) then ASTM C 39 (immersion), ASTM D 4843 (wet-dry)	TBD	Is this a good measure of durability for materials disposed of in controlled facilities?
Full-scale demonstration	*Compression and immersion tests on full-size samples	TBD	NRC guidelines require demonstration of scalability to full-size waste containers. Are the tests appropriate?

* Tests cited in NRC guidance¹

** Tests specified for RCRA-regulated wastes that are hazardous by characteristic

a. EPA procedures are published in Test Methods for Evaluating Solid Waste, SW-846, third edition (revised November 1990), U.S. EPA, Washington, D.C., 1990.

ANS procedures are published by the American Nuclear Society, LaGrange Park, Illinois.

ASTM procedures are published by the American Society for Testing and Materials, Philadelphia, Pennsylvania.

Table 2.3. Additional tests potentially applicable for leach resistance and chemical durability

TEST	CONDITIONS ^a	COMMENTS
ANS 16.1 ²	Intact cylindrical sample exposed to deionized water or synthetic sea water at volume:surface area=10 cm (3.9 in.) with leachant exchanges 10 times over 90 days.	To simulate diffusion-controlled dissolution; used to calculate apparent diffusion coefficient and leachability index.
TCLP ³	Crushed sample exposed to acetate solution (pH 3 or 5) at liquid:solid=20 for 18 hr.	Regulatory test for RCRA-regulated wastes.
EP toxicity ⁴	Crushed sample exposed to acetate solution (pH 3 or 5) at liquid:solid=16 for 24 hr.	Former regulatory test for RCRA-regulated wastes. May still be allowed for Land Disposal Restriction (LDR) testing.
Cal. WET ⁵	Crushed sample exposed to citrate solution (pH 5) at liquid:solid=10 for 48 hr. Deionized water is used to leach Cr ⁶⁺ .	State of California regulatory test for hazardous wastes.
MEP ⁶	Crushed sample treated according to EP, then extracted with synthetic acid rain until decline in leachate metals concentration.	Intended to simulate response to environmental exposure.
EE ⁷	Finely crushed sample is exposed to deionized water at liquid:solid=4 for 7 days.	Intended to measure maximum metal dissolution under mild conditions.
ANC ⁸	Finely crushed sample aliquots exposed to nitric acid solutions of different strengths at liquid:solid=3 for 48 hr. pH is measured; metals may be measured.	Measures the buffering capacity of the waste or waste form. If metals are analyzed, data can be used to construct an effective solubility curve.
SCE ⁹	Finely crushed sample is exposed to 5 solutions of increasing acidity at variable liquid:solid ratios.	Intended to measure the ease of dissolution of 5 metal fractions; the fractions are operationally defined but supposed to relate to groups of chemical species. Unsuitable for arsenic and mercury according to developers.
DLT ¹⁰	Variant of ANS 16.1 ³ with sample-dependent volume:surface area ratio and leachant exchange intervals.	Modification intended to better meet conditions for diffusion-controlled leaching; identifies occurrence of reaction and convection processes.
MCC-1P ¹¹	Monolith sample is exposed to a leaching solution at volume:surface area=10:1. Temperature and exposure times vary.	Intended for screening and comparison of alternative formulations. Developed for high-level radioactive waste.
ALT ¹²	Intact cylindrical sample leached in de-ionized water at elevated temperatures for 11 days.	Elevated temperatures accelerate leaching conditions to obtain more rapid results. Model confirms leaching mechanism remains consistent and allows prediction of long-term leachability.
PCT ¹³	Method A: -100+200 mesh sample exposed to ASTM-Type I water at 90°C (194°F) for 7 days at liquid:solid=10. Method B: Allows use of varying leachant types, durations, temperatures, and liquid:solid ratio.	Intended to evaluate the chemical durability of homogeneous and devitrified glasses to evaluate product consistency. Developed for high level waste.

a. All liquid to solid ratios are for liquid volume in mL and solid weight in g.

waste guidance. However, these tests may not ensure compliance with the goals of the regulatory agencies, namely the control of contaminant release at concentrations that could be deleterious to human health or the environment. Further, the tests may yield conflicting data (e.g., ANS 16.1 vs. TCLP) or may emphasize properties that have little to do with true waste form performance within the full waste control system at a specific site.

To date there has been too little feedback between laboratory testing programs and development of performance assessment methodology, to the extent that PA methods for LLW disposal generally assume that the waste form has no retarding effect on contaminant release. Closing the loop will entail validation studies to convert laboratory data to equivalent field rates for physical and chemical changes in the waste form.

As research and applications continue, performance criteria will be refined to the minimum set that ensure the long-term environmental stability of the specific field-disposed waste form. Documentation of waste form performance during this process will contribute to regulatory acceptance of waste forms and disposal plans as DOE proceeds through its site cleanup program.

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10. *Environment Canada and Alberta Environmental Center, "Dynamic Leach Test," Investigation of Test Methods for Solidified Waste Evaluation — A Cooperative Program, Appendix B: Test Methods for Solidified Waste Evaluation, EPS 3/HA/8, Environment Canada, 1991.*
11. *Pacific Northwest Laboratory, "Materials Characterization Center Static Leach Test," Method MCC-1P, Pacific Northwest Laboratory, 1984.*

3. FINAL WASTE FORM OPTIONS

The final waste forms chosen for this study are those which are most commonly used and for which there are readily available data. These were deemed the most favorable options for solidifying or stabilizing LLMW throughout the DOE system. The following sections provide descriptions of each waste form.

3.1 GLASS WASTE FORMS

Glass waste forms are normally obtained by mixing one or more waste streams containing radioactive and hazardous inorganic chemical compounds with glass-forming materials and melting these materials during a vitrification process. The glass forming materials may be commercially melted glass frit, select chemicals, or in some cases, materials which are present in the waste streams. Glasses are not composed of discrete molecules, but are three-dimensional, continuous networks.¹ Generally the oxide of silicon (SiO_2) is the major component and provides the three-dimensional network. This adaptable network structure strongly influences the glass waste form character and properties.

Glass may be formed by thermal processes or by non-thermal processes such as vapor deposition, solution hydrolysis, or gel formation. Thermally-formed glasses as discussed in this report are produced by fusing or melting crystalline materials and/or amorphous materials at elevated temperatures to produce liquids. These liquids are subsequently cooled to a rigid condition without crystallization. Many waste glasses also have one or more crystalline phases distributed in the glass. From an engineering standpoint, what distinguishes glass from crystalline substances is the lack of a definite melting point temperature. When glass is heated above a transition temperature, it will gradually deform and, at high enough temperatures, form a viscous liquid. While most waste glasses are based on the silica network, other network forming systems have been considered for specific waste streams.

The glass waste form discussed in the vast majority of references is borosilicate glass ($\text{B}_2\text{O}_3\text{-SiO}_2$) as employed in the high-level waste program.^{2,3,4} Information regarding the properties and characterization of this type of glass waste form is readily available. The waste form usually contains less than 30 wt% of waste solids; however, the vitrification process generally reduces the waste volume significantly. Specific waste streams can be added at higher temperature levels and, under conditions where the waste contains sufficient glass formers, a glass containing only waste can be produced. A wide variety of glass compositions may be suitable for glass waste forms and may provide advantages for the vitrification of a particular waste stream. While the waste type considered in much of the referenced work was high-level waste, some additional references include low-level, mixed, and transuranic (TRU) waste.

Numerous efforts have been conducted to investigate other glass compositions (e.g., phosphate (P_2O_5),⁵ sodalime silica ($\text{Na}_2\text{O-CaO-SiO}_2$),⁶ aluminosilicate ($\text{Al}_2\text{O}_3\text{-SiO}_2$) glasses⁷) for waste solidification. However, the extensive information database for the borosilicate glass waste form, its long-term development over the last thirty years, and its

present acceptance throughout the world potentially make the borosilicate waste form uniquely advantageous for many waste stabilization problems.

All the components take on one of three basic roles in the glass structure: network formers, intermediates, or modifiers. The network formers, such as silica, boria, and phosphate (SiO_2 , B_2O_3 , and P_2O_5), provide the basic three-dimensional skeletal network which gives the glass waste form its long-term leach resistance, mechanical strength, and durability. Other oxides, the intermediates, (Al_2O_3 , PbO , TiO_2 , etc.) can substitute for the network formers, but only to a limited extent. The modifiers (Na_2O , CaO , etc.) are more loosely associated with the network formers and tend to disrupt or break the interconnected network bonds. Their presence generally lowers the glass viscosity and permits vitrification and forming at reasonable melt temperatures. Since the modifiers can also reduce some of the advantageous glass properties such as strength and leach resistance, glass formulation development consists of a series of trade-offs, balancing physical properties with processing requirements.

The thermal vitrification process involves heating the materials to temperatures in excess of 1000°C (1832°F). At these temperatures any free liquid or organic material is evaporated, pyrolyzed, or oxidized and the residual inorganics are vitrified to form a molten glass. Many metallic compounds of environmental concern can be incorporated into a glass matrix and are commonly used as colorants in glassmaking.¹ The ability of glass to incorporate small amounts of metallic compounds in controlled quantities has a long history: selenium and arsenic are used as decolorizers for clear glass bottles; chromium gives some green glass its color; and lead oxide at levels up to 30% is found in lead crystal glass.⁸ Hazardous constituents may also be immobilized without direct chemical interaction with the glass network. The materials which do not interact chemically, e.g., pyrolyzed carbon or metal, may be surrounded by a layer of vitrified material and encapsulated, as the melt cools. After the vitrification process, the waste glass melt can be cooled, formed into geometric shapes, poured into containers to form monoliths, or quenched to form irregular particles. Because glass has the ability to accept a wide variety and amount of radioactive or hazardous materials and because its physical properties are normally constant with time, glass has been selected to stabilize a variety of waste streams. The EPA has determined that vitrification is the Best Demonstrated Available Technology (BDAT) for high-level nuclear waste⁹ and for non-waste waters containing arsenic.¹⁰

Thermal vitrification resulting in a glass final waste form can be accomplished by a wide variety of processes. These vitrification processes include fossil fuel combustion, electric heating (joule), plasma arc melting, graphite arc melting, in situ vitrification, and induction and microwave heating. This wide variety of technologies may provide advantages with specific waste streams.^{1,11}

3.2 HYDRAULIC CEMENT WASTE FORMS

Portland cement and similar materials (hydraulic cements) are the solidification agents which are most often referenced in available LLW solidification literature. The hydraulic cements can exhibit physical encapsulation and/or chemical bonding

characteristics. These are dependent upon the cementing agent, water content, and waste stream involved. A list of hydraulic cement base agents is presented in Table 3.1.

Table 3.1. Cement-based waste form solidification materials

Portland Cement	Type I - general use Type II - general use plus moderate sulfate resistance Type III - high early strength Type IV - low heat of hydration Type V - high sulfate resistance Plug - early set, expanding cement Masonry - high workability (highly alkaline)
Gypsum Cement	Plaster of Paris Envirostone®
Grout (variable)	--
Slag Cement	--
Polymer-Modified Cement	Latex cement Polymer-impregnated cements (concretes) Epoxy-cement mixtures or combinations Polymer-cement mixtures or combinations
Other	Alumina-based cement Silicate cement Lime or lime-fly ash mixtures Pozzolan cement

Portland Cement

Hydraulic cements include the general portland cements comprised primarily of calcium silicate species. These cements mix with water to form a basic slurry exhibiting an initial pH of 11 to 14, depending upon the type of mix. Masonry cement contains free lime in addition to the portland cement component and is the most basic of the cements. Portland cements readily combine with most neutral and basic pH materials to produce a strong, monolithic product. Strongly acidic waste components require at least partial neutralization prior to solidification. The cements, particularly masonry cement, are inherently basic and can be used to neutralize and solidify some acidic materials in a single step.

Gypsum Cement

Gypsum is a calcium sulfate mineral. Plaster of paris is a typical gypsum cement, and has 0.5 mole water per mole of reagent. It reacts with water to form a gypsum-type compound (calcium sulfate with 2 moles water per mole of reagent). Plaster of paris has a neutral pH when mixed with water. It can be used to immobilize ammonium salts, and it encapsulates the salt or the dissolved liquid in its neutral matrix. The ammonium ion is stable (does not decompose) in the neutral matrix and the mixture solidifies without the loss of any appreciable ammonia gas. It will solidify other neutral and moderately acidic or basic compounds without affecting the general gypsum product characteristics. Gypsum typically sets faster than portland cement, but produces lower strength products.

Grout

Grout is a pumpable mixture containing a cement base and other materials, such as clay and flyash, to increase radionuclide or hazardous chemical retention. Grout contains more water and solidifies more slowly than the typical portland cement. Mechanical strengths such as compressive strength are typically lower for grout than for cement. Grout is used to provide higher waste loadings and better waste retention properties, and is designed for pipeline delivery or transport.

Slag Cement

Slag cement (blast furnace slag cement) is a by-product of the steel industry. It is a high-temperature fired material and looks much like flyash. Unless being used directly to solidify highly caustic materials, it requires an initiator (caustic-type compound), generally portland cement or lime. Its solidification time and other characteristics are very similar to those of cement. It has been shown to exhibit better waste retention properties and leach performance than similar portland cement products, but generally exhibits lower strength.

Polymer-Modified Cements

Portland cement products, being naturally basic, are susceptible to degradation by acids and to a lesser extent by certain salts. This is true in applications such as concrete tanks, floors, and buildings. Cement in these applications can be modified with polymer materials to seal it and make it less penetrable. This type of treatment can be used to reduce water penetration and reduce leachability. Polymer modified cement waste products are expected to exhibit improved leach performance, better waste retention properties, and even better physical strengths. Polymer-modified cement can be used to achieve many of the positive characteristics of organic polymers and is still fire resistant, since the bulk of the matrix is non-flammable.

Other

Other hydraulic cements include pozzolan cement which is a portland cement base material ($\approx 75\%$) with an added pozzolanic material (25%) such as volcanic ash. It can exhibit higher compressive strengths and sometimes better waste retention than some of the other cements, and it is generally not as basic. Since pozzolan cement already has ash in it, it should not be used for immobilizing ash waste; conversely waste ash can potentially be blended with portland cement to make a pozzolanic material that could be used to solidify other mixed waste materials.

Alumina cements are also available. These exhibit the best fire protection properties of the hydraulic cements, have different material compatibilities (sometimes better), and generally have lower waste loadings. The alumina cements are usually more expensive and less commonly available. Also, lime and other natural cements are available. They are used for special purposes or applications. They are generally used when the more common cements are not compatible with the waste matrix. Lime and other natural cement products exhibit lower compressive strengths than portland cement.

3.3 SULFUR POLYMER CEMENT WASTE FORMS

Sulfur polymer cement (SPC)^a and modified sulfur cement are different names for the same substance, which consists of 95 wt% sulfur, 2.5 wt% dicyclopentadiene, and 2.5 wt% oligomers of cyclopentadiene.^{12,13} In 1990, the American Society for Testing and Materials (ASTM) issued their specification for SPC¹⁴, entitled "Standard Specification for Sulfur Polymer Cement For Use in Chemical-Resistant, Rigid Sulfur Concrete." Since then, industry has generally dropped the term "modified sulfur cement" and uses "sulfur polymer cement" (SPC). SPC is available commercially under the trade name Chement 2000®. Because of SPC's unusual physical and chemical properties, DOE and the Commission of European Communities began testing and developing SPC as a solidification and stabilization agent for radioactive and hazardous wastes.

SPC is a thermoplastic ceramic that starts softening at 110 – 115°C (230 – 239°F) and starts melting at $\approx 120^\circ\text{C}$ (248°F). It reaches optimum pour consistency at 135°C (275°F) with a viscosity of 0.025 – 0.050 Pa-s (25 – 50 cp), roughly equivalent to cold automobile engine oil. It has a maximum safe operational mixing-and-pouring temperature of 150°C (302°F). Upon cooling, SPC with normal construction aggregate, achieves a strength of ~ 27.6 MPa (4,000 psi) and within two years has a strength of nearly three times that.¹⁵ When solid SPC is subjected to sustained high temperature, it will become molten again and then regain its strength upon cooling, as it did during the initial heating-cooling process.

^aSulfur polymer cement in its original flaked cement form, in its molten form, in its molten form with waste added and in its final solid concrete form are all referred to as SPC. A different formulation of 'SPC' is commercially manufactured in Canada under the trade name Sulfurcrete®, but it has not yet been investigated and is not included herein.

SPC will not tolerate water in the mix; when water is in the waste, steam vents are formed in the concrete and it is weakened.¹³ For this reason, a waste product to be solidified should be heated to as much as 200°C (392°F) to evaporate the water. That heat is not wasted because it is used to help raise the SPC to pour temperature when the two are combined.¹⁶

By U.S. Department of Transportation (DOT) and United Nations (UN) standards, solid SPC is not flammable. SPC will not support combustion. If a torch is directed to its surface, SPC will burn and form a self-extinguishing black char that puts out the flame.^{13,17} Any time the torch is removed, the flame will self-extinguish. During pouring operations, normal safety procedures will prevent any flammability or explosive condition.^{18,19,20,21,22}

Linear shrinkage is 0.1%, slightly greater than that of PCC. SPC is a durable, high-strength concrete that is resistant to abrasion and to attack by most acids, salts, and sulfates that destroy hydraulic concretes. It is advantageous to use where exposure to high concentrations of mineral acids, corrosive electrolytes, salt solutions, or corrosive atmospheres in general is expected.^{17,23,24}

3.4 CRYSTALLINE CERAMICS, GLASS-CERAMICS, AND "CHEMICALLY-BONDED" CERAMICS

In American usage, the term ceramic refers to "any of a class of inorganic, nonmetallic products which are subjected to a high temperature^b during manufacture or use."²⁵ This definition includes crystalline ceramics, glass,^c and glass-ceramics, which are composed of crystals within a glass matrix. The term "ceramic" also includes the so-called chemically-bonded²⁶ ceramics which are manufactured at lower temperatures, but can be used at high temperatures. These materials are formed by chemical bonding at low temperatures as opposed to the high temperature sintering or fusion of conventional ceramics.²⁷

The distinction between crystalline ceramics and glasses is in their atomic structure: crystalline materials exhibit a long-range ordered structure, while glasses have an amorphous structure that shows only short-range order. While glasses often exhibit high chemical durability, and indeed are found in nature with ages of millions of years, they are thermodynamically unstable with respect to conversion to crystalline forms of the materials of which they are composed. Given extended times at elevated temperatures [above about 450° – 500°C (842° – 932°F)] or contact with water over long periods, they will convert to crystalline minerals.

^bHigh temperature usually means a temperature above a barely visible red, approximately 540°C [1,000°F].²⁵

^cGlass is defined as "an inorganic product of fusion that has cooled to a rigid condition without crystallizing."²⁵

Since glasses have been discussed in Section 3.1 and in later sections of this report, the discussion here is limited to crystalline ceramics formed at high temperatures, chemically-bonded ceramics formed near room temperature or somewhat above, and glass-ceramics formed by melting and controlled heat treatment.

Historically, ceramic materials were made from clay or similar materials and were fired at a high temperature to produce a durable product. Modern ceramics cover the full range of non-metallic crystalline materials and are produced by a range of fabrication methods. The most common processes used for crystalline ceramic waste forms have been either hot pressing, or cold pressing and sintering^d of powders. Glass ceramics are made by melting, followed by controlled heat treatment to produce partial crystallization. Chemically-bonded ceramics are formed by hydration reactions that occur at lower temperatures.

The first application of ceramics to the problem of containing waste radionuclides was attributed in 1953 to Ginell at Brookhaven National Laboratory, who proposed incorporating waste in montmorillonite clay by cation exchange and firing at 1000°C (1832°F) to render the material inert to further ion exchange reactions. According to Hatch,²⁸ the motivation was to confine the radioactive material by chemical, rather than mechanical means, in a product of high stability.

Work since that time has explored a variety of ceramic materials, primarily for incorporation of high-level nuclear waste. Ideally, in designing a ceramic waste form, one would like to be able to choose a chemically durable crystalline phase or phases that will incorporate the radionuclides within the crystal structure. However, there are certain constraints: the overall composition of the waste stream, including non-radioactive components; the desire to minimize the total waste form volume (and thus the need to use high waste loading); and, the dictates of crystal chemistry and thermodynamics in determining the solubilities of the radionuclides in the various phases and the compatibility of the phases with each other during the high temperature fabrication step. Approaches to developing ceramic waste forms have thus varied in the degree to which they have attempted to direct the radionuclides into durable phases of the ceramist's choosing, or, alternatively, to attempt to modify the waste stream composition by augmenting it with minimum amounts of additives, and thereby form phases which may not be as chemically durable (but still satisfactory) in order to achieve higher waste loading. An example of the former approach is SYNROC,²⁹ which is based on highly durable titanate phases found in gem gravels that have survived for hundreds of millions of years. An example of the latter is tailored ceramic,³⁰ which can achieve a waste loading of up to 85%.

Natural analog minerals can be found for many of the minerals in ceramic waste forms. Their ages and approximate history in terms of temperature, chemical environment, and natural radiation dose can often be determined. These analogs are very helpful in making long-term projections of waste form behavior.

^dTo sinter means "to densify, crystallize, bond together, and/or stabilize a particulate material, agglomerate, or produce by heating or firing close to but below the melting point; this often involves melting of minor components or constituents, and/or chemical reaction."²⁵

Among the possible crystalline ceramic materials, those that have received the most study as host materials for radionuclides have been the oxides. Four main classes of crystalline-oxide ceramic waste forms have been developed: silicate-based, aluminate-based, phosphate-based, and titanate-based. Limited efforts to develop chemically-bonded and glass-ceramic waste forms have also been conducted.

Silicate-Based Ceramics

The most developed silicate-based ceramic waste form was called Supercalcine, and was developed by McCarthy and co-workers at Penn State.³¹ Supercalcine formulations included such phases as pollucite, scheelite, fluorite, apatite, baddeleyite, corundum, spinels, and perovskites. They were formed by firing at temperatures over 1000°C (1832°F) with high oxygen partial pressures. This led to concerns about volatilization of elements such as Cs, Tc, and Ru. In addition, the use of silicates, molybdates, and phosphates led to the generation of a significant unoptimized soluble glass phase, which made Supercalcine susceptible to phase-specific dissolution in water.³⁰ As a result, work on silicate-based ceramics has not been pursued.

Aluminate-Based Ceramics

Aluminate-based ceramic waste forms were developed by Rockwell International under the name tailored ceramics.³⁰ The phases present included corundum, spinel, magnetoplumbite, uraninite, nepheline, and a glass phase. The original formulation was made to incorporate the high-aluminum type of SRS high-level defense waste. When higher-iron waste streams were considered, it was not possible to form a satisfactory phase to incorporate Cs, Sr, and Ba, nor could a highly stable crystalline phase be formed to incorporate the alkali in the waste stream. This led to the development of a combined aluminate-titanate waste form known as RSC-S29. Its phases included zirconolite, magnetoplumbite, magnetite, spinel, murataite, and a small amount of glass phase.³²

Phosphate-Based Ceramics

Phosphate-based ceramic waste forms have been developed by Boatner and co-workers at Oak Ridge³³ and by researchers at Penn State.³⁴ They have included monazite, sodium zirconium phosphate, sodium titanium phosphate, and berlinite (AlPO_4).

Titanate-Based Ceramics

Titanate-based ceramic waste forms have been developed by Sandia National Laboratories (SNL),³⁰ by Ringwood and co-workers in Australia,²⁹ and by Lawrence Livermore National Laboratory (LLNL).³⁵ They capitalize on the extremely high durability of titanate minerals and their ability to incorporate radionuclides of concern. SYNROC-C was developed to incorporate high-level waste from the reprocessing of nuclear power reactor fuel. It is a fine-grained, polyphase crystalline ceramic composed

primarily of the minerals hollandite, zirconolite, perovskite, and titanium oxides and/or minor calcium-aluminum titanates, plus small amounts of metallic alloys and a calcium-rich phosphate. The first three phases are intentionally chosen to incorporate radionuclides. The titanium oxides serve as a buffer to ensure that sufficient Ti is present. The metallic alloys incorporate the noble and reduced metals, and the phosphate incorporates the phosphorous present in Purex (Plutonium and Uranium Extraction) waste streams.

SYNROC-D³⁵ was developed to incorporate SRS composite high-level defense waste and was selected as the alternative to borosilicate glass for this purpose. SYNROC-D is also a fine-grained polyphase ceramic. Its phases are zirconolite, perovskite, spinel, nepheline, and a silicate glass.

Glass-Ceramics

Glass-ceramic waste forms³⁶ have been studied in Germany, the U.S., Japan, Sweden, the U.S.S.R., and Canada. In the U.S., the main efforts have been carried out at the Pacific Northwest Laboratory (PNL)³⁷ and the INEL³⁷ on waste forms known as basalt glass ceramics and iron-enriched basalt. The latter is a fusion-cast partly-crystalline ceramic prepared from oxides of Si, Al, Fe, Ca, Mg, Ti, K, and Na, together with non-radioactive simulants or actual wastes. This waste form has been studied for use with TRU wastes and with defense high level wastes from the Idaho Chemical Processing Plant (ICPP) and the SRS. The crystalline phases in this glass-ceramic material have included spinel, plagioclase, augite, fluorapatite, zircon, fluorite, cristobalite, and mullite. The glass is an aluminosilicate glass. The material is melted at 1,400 – 1,500°C (2,552 – 2,732°F), cast, and heat-treated at 1,000 – 1,100°C (1832 – 2,012°F) to form the crystals. The Canadian glass ceramic work has focussed on sphene-based material, which is composed of oxides of Na, Al, Ca, Ti, and Si, and nuclear wastes.

Chemically-Bonded Ceramics

Chemically-bonded ceramics²⁶ are formed at temperatures near room temperature. The character of the bonding after heating to relatively low temperatures is dominated by ionic and covalent bonds, as compared with the weaker Van der Waals and hydrogen bonding that is dominant in hydraulic cements.²⁶ Aside from variations of traditional hydraulic cement compositions, it appears that the most attention within this category of materials has been placed on phosphate-bonded ceramics.³⁸ Phosphate cements are commercially available and have been applied to heavy-metal-containing wastes.^{39,40}

3.5 ORGANIC BINDERS

Organic binders are being studied extensively in the U.S. and in Europe for immobilization of low-level wastes generated at nuclear power plants, research laboratories, and industrial production facilities. Many candidate organic binders are already produced commercially, while others remain in various developmental stages.

Organic binders are predominantly polymeric materials comprised of small, simple repeating units (monomers). They are synthesized by polymerization processes such as addition or condensation mechanisms which yield high molecular weight macromolecules that consist of hundreds of monomer units.⁴¹ The degree and rate of polymerization can be controlled by varying the content of catalysts (initiators), accelerators, inhibitors, and by varying processing parameters such as temperature and pressure.

The macromolecular structure that results from polymerization processes can vary substantially. In some cases, polymerization results in linear repetition that gives rise to long polymer chains. In other cases, the chains are branched or cross-linked to form three-dimensional network structures. Either of these network structures provides encapsulation of the wastes and gives structural stability to the waste form.⁴²

Overall physical, chemical, and mechanical characteristics of the binder material are dependent on the polymer structure and the interactions between the polymer chains.⁴² Branched chains are formed as a result of side reactions during polymerization and are essentially discrete molecules, while cross-linking or formation of strong chemical bonds between polymer chains takes place in the presence of crosslinking agents.⁴² Small chain segments and/or foreign atoms lead to crosslinking of polymer chains. Crosslinking is known to result in a network structure with better chemical and mechanical properties than those of branched polymers.

Organic binders are categorized as thermoplastics or thermosetting polymers. Thermoplastics (linear or branched polymers) flow at elevated temperatures [$\approx 80 - 180^\circ\text{C}$ ($176 - 356^\circ\text{F}$)] and are easily molded. Thermoplastic materials and their associated technologies have been extensively studied and have been in use in various industries for over 50 years. Associated processes for solidification are relatively simple and are readily adaptable. On the other hand, thermosets have crosslinked polymer chains and set at room or elevated temperatures to form rigid solids that do not flow. For polymerization, thermosets require additional constituents such as catalysts and promoters.⁴³

Table 3.2 lists common thermoplastic and thermosetting binders that have been identified as candidates for final waste forms. Each of these candidate materials possesses a unique set of properties that may be suited for a given application. Only extensively studied thermoplastic (polyethylene and bitumen) and thermosetting (vinyl ester styrene, epoxy, and urea formaldehyde) binders possessing superior properties will be discussed.

Organic binders contain the waste material by microencapsulation.⁴⁴ The waste is surrounded, immobilized, and isolated from the environment by the highly impervious network structure of polymers.⁴⁴ For thermoplastics, because there is no direct chemical interaction between the waste and the organic binder, various waste types can be successfully incorporated. This is especially advantageous for containment of complex mixed wastes. However, thermosets can be limited in their use because of the possibility of interference with polymerization by waste stream chemicals.

Table 3.2. Various organic binders for final waste forms

THERMOPLASTIC SYSTEMS	THERMOSETTING SYSTEMS
Polyethylene	Polyesters (vinyl ester styrene)
Bitumen	Epoxy
Polyvinyl chloride	Urea formaldehyde (UF)
Polymethyl methacrylate	Polyurethanes

Thermoplastics and thermosets have excellent chemical tolerance and are compatible with various low-level waste streams (both aqueous and solid) such as boric acid concentrates, ion exchange resins, alkaline waste solutions, and sludges. In general, organic binders incorporated with a variety of waste streams and loadings have exhibited excellent nuclide retention and leach performance properties. In particular, bitumen has been found to provide better retention characteristics for arsenic compared to some other binder systems.⁴⁵

Both thermoplastics and thermosets exhibit high waste loading capacities. Waste loadings of 40-50 wt% are common for organic binders, and waste loadings as high as 70% have been achieved in some systems. For thermoplastics, there is a large volume reduction of aqueous wastes due to evaporation of contained water during elevated temperature processing. This results in a high waste volume efficiency for these binders. Moreover, because of the low processing temperatures, organic binders do not generate secondary waste streams with volatile metals.

Compressive strengths of organic binders (both thermoplastics and thermosets) are lower than those of glass and some cement waste forms, and range between 13.8 and 55.2 MPa (2,000 and 8,000 psi) for a variety of waste types and loadings. Furthermore, thermosets have higher strengths than thermoplastics because of their crosslinked polymer chain structure. Thermoplastics lose their mechanical integrity on heating, but regain it on cooling.

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4. SUMMARIES OF PERFORMED TESTS

4.1 GLASS WASTE FORM TEST SUMMARIES

Prior to the selection of borosilicate glass as the waste form for high-level wastes at SRS, DOE initiated a program to evaluate a number of alternative waste forms, including other glasses, ceramics, concretes, cements, metals, and composite materials. After a two-year multi-laboratory development program, two waste forms were chosen for final consideration. These waste forms were the crystalline ceramic SYNROC-D^{1,2,3} and the reference borosilicate glass. The waste form properties of the borosilicate glass are briefly described as follows:

- The compressive strength for borosilicate glass was given as 550 MPa (80,000 psi). This is similar to the compressive strength quoted for ceramics and is the same order of magnitude as many geologic formations. Glass can be formed into many shapes, but when it is cast as a large monolith some cracking can be expected during cooling. This may increase the surface area of the glass by about five times. When the glass is impacted with an energy density of 10 joules/cc the amount of fines [$<1\text{E-}05\text{ }\mu\text{m}$ ($<10\text{ micron}$)] will increase by 0.14 to 0.18 wt%.
- As long as the temperature of the glass is maintained below 450 – 500°C (842 – 932°F) there is little change in the glass waste form, as atomic diffusion is negligible. Some crystallization may begin at higher temperatures. There is essentially no weight loss up to temperatures of 800°C (1,472°F). The rate of structural change for glass is extremely low at normal environmental temperatures.
- Extensive radiation damage studies on borosilicate glass, including doping tests with Pu-238 and Cm-244, indicate that the performance of high-level waste glass should not be affected significantly by self-irradiation at design concentrations of actinides for periods of one million years or more. The change in density during this period is $\pm 1.5\%$. Self irradiation, itself, has little or no effect on leaching or mechanical properties; however, irradiation can change the pH of surrounding solutions, which can affect the leach rate. MCC-6 is the suggested radiation test for high level waste and is considered a severe test, with approximately 3×10^{18} alpha decays/cm³.^{4,5}
- The leaching properties of borosilicate glass and SYNROC-D were compared for Cs, Sr, U, and eight other elements under a variety of test conditions. Comparative leaching data are available for the 28-day MCC-1 test. Neither glass nor SYNROC-D was superior in leach resistance for all the principal radioactive waste elements. However, on the average, the the leach resistance of SYNROC-D was slightly better for the elements studied. SYNROC-D is significantly better than borosilicate glass for U retention, but borosilicate glass was much better for Sr. Differences between the two for Cs retention are small and depend on waste composition.¹ Both were found to be acceptable for high-level waste disposal.

A large-scale evaluation of the borosilicate waste glass in conditions similar to MCC-1 was carried out at SRS.⁶ Combined scale-up, glass cracking, leached surface area estimation, and surface roughness effects increase the leach rate by less than a factor of three. This is in reasonable agreement with and substantiates the results of the small-scale test data, which preceded this work.

A thermodynamic approach for prediction of glass durability was refined at SRS.⁷ When the calculated free energy of hydration is plotted for a wide variety of glass composition, including natural, medieval, and nuclear waste glasses, against the release of structural silicon into deionized water in a standard test, a linear relationship is found. However, glass compositions which cause pH excursions to values greater than ten must have an additional free energy term. These relationships permit the durability of new glass compositions to be predicted. An improved Product Consistency Test (PCT) method was found to provide a more controlled evaluation and has been used to compare new waste form glasses.^{8,9}

A number of tests are being carried out to determine the long-term behavior of borosilicate glass in repository conditions.^{10,11} SRS borosilicate glasses were buried for up to two years in granite at the Stripa mine in Sweden, with other nuclear glasses in salt at the Waste Isolation Pilot Plant in New Mexico and in limestone at Ballidon, England. Glass samples have been removed periodically and examined by various analytic experts throughout the world. The glasses selected represent the expected range of glass compositions for the high-level waste. While the glass compositions and geologic conditions were very different, the leaching depth for all samples was within a range of $5\text{E-}07 - 4\text{E-}06 \mu\text{m}$ (0.5 - 4 microns) after 24 months. These field data supported laboratory findings which indicated that the chemical durability of the SRS waste glass was not only very good, but actually improved with time.

A recent evaluation of the simulated high-level waste glass containing two to three times the projected levels of Cr, Pb, Ba, Ag, Se, and Cd expected was made by the TCLP and EP Toxicity Tests. The results indicated that this glass did not fail the RCRA characteristic test for toxicity.¹²

There are many hundreds of papers on the interactions of both simulated and radioactive high-level waste glass with the surrounding geology and environmental conditions.^{13,14,15,16,17,18} The remaining test data cited here consider mixed and low-level waste glass evaluation.

The commercial glass industry has vitrified many glass compositions doped with varying amounts of toxic and non-toxic elements in order to improve or modify the glass character. An excellent review of chemical solubility in glass was presented by Volf.¹⁹

Recent developments with in situ vitrification (ISV)^{20,21} indicated that vitrification of a mixture of toxic materials and soil together produced a vitrified block which, when tested by TCLP, was several orders of magnitude below regulatory limits. While the resultant waste form was considered non-hazardous, additional engineering concerns about the offgas system remain. A summary of TCLP data for various glasses is presented in Table 4.1.²² Data are not directly comparable, but are shown to verify that, in general, vitrification products pass toxicity characteristic limits.

Table 4.1. TCLP leach data for selected processes and selected metals

METAL	GLASS MELTER	KILN/VIT. PROCESS	ISV GLASS	ISV METAL	TCLP LIMITS
Arsenic	<0.02	<0.01	<5	<5	5.0
Barium	<0.05	<0.175	<0.05	<1	100.0
Cadmium	0.007	0.015	<1	<1	1.0
Chromium	0.03	0.825	<1	2.7	5.0
Lead	<0.05	0.15	<1	<1	5.0
Mercury	<0.0002	0.00035	<0.03	<0.03	0.2
Silver	<0.01	0.01	<0.1	<0.1	5.0

NOTE: Values are expressed in ml/kg.

Samples of K-65 residue from the processing of pitchblende ores were vitrified on a laboratory scale.²³ The residue contained radium, U, daughter products, and heavy metals (primarily lead). The materials also emitted radon gas at a rate 2500 times the EPA limit. After vitrification to a soda-lead-barium silicate glass, the glass passed the TCLP tests, the volume was 39% that of the original material, and the radon emanation rate was reduced by a factor of 33,000.

The development of combined soil washing and vitrification was recently reported. Storm sewer sediment from the Y-12 Facility at Oak Ridge was contaminated with Hg, U, Th, and PCBs. Pre-treatment by washing the soils appears to have an economic advantage. The residual material will be vitrified.²⁴

Secondary lead slags and mattes were formulated into glass compositions in order to stabilize the material with regard to the lead release levels as established by the EPA TCLP. Vitrification and composition adjustment reduced lead release by about 50 times.²⁵

Vitrification may be an attractive means of treating municipal solid waste ash.²⁶ Vitrification provided an 80% volume reduction, formed a homogeneous glass, and was economically favorable with regard to transport and landfill.

Existing research and development (R&D) on high-temperature metal processing in glass melters indicates that glass may not be able to capture a high percentage of the metal contaminants during waste form processing. The percentage of metals that remain in the glass is dependent on factors such as the melter temperature, chloride content, carbon content, metal volatility, presence of a cold cap, and excess air.

Table 4.2^{19,27,28} lists the volatile toxic metals and metal compounds by boiling point and by inclination to volatilize. The degree of metal volatilization can be divided into the following four categories:

Table 4.2. Boiling points of toxic metals and their compounds in common glass melts

Low <10% Volatilization ^a		Medium <40% Volatilization ^a		High <90% Volatilization ^a		Total >99% Volatilization ^a	
TCLP Metal	Boiling ^b Point °C (°F)	TCLP Metal	Boiling ^b Point °C (°F)	TCLP Metal	Boiling ^b Point °C (°F)	TCLP Metal	Boiling ^b Point °C (°F)
Ba	1,640 (2,984)	Cd	765 (1,409)	As	613 (1,135)	Hg	357 (675)
BaCl ₂	1,560 (2,840)	CdCl ₂	960 (1,760)	As ₂ S ₂	565 (1,049)	HgCl ₂	302 (576)
BaO	2,000 (3,632)	CdF ₂	1,758 (3,196)	As ₂ O ₃	457 (855)	HgF ₂	650 (1,202)
BaF ₂	2,137 (3,878)	CdO	1,559 (2,838)	Se	685 (1,265)	HgO	500 (932)
Cr	2,672 (4,841)	Pb	1740 (3,164)	SeC ₂	126 (259)	---	---
Cr ₃ C ₂	3,800 (6,782)	PbF ₂	1,290 (2,354)	SeOCl ₂	176 (349)	---	---
CrO ₃	4,000 (7,232)	PbCl ₂	950 (1,742)	SeOF ₂	124 (255)	---	---
CrF ₃	1,200 (2,192)	PbO	1,472 (2,682)	SeO ₂	317 (603)	---	---
CrCl ₃	1,300 (2,372)	PbS	1,281 (2,338)	---	---	---	---
Ag	2,212 (4,013)	Pb ₃ O ₄	1,300 (2,372)	---	---	---	---
AgCl	1,550 (2,822)	---	---	---	---	---	---
AgF	1,159 (2,118)	---	---	---	---	---	---
Ag ₂ O	300 (572)	---	---	---	---	---	---

a. Volatilization in glass melts depends on many other factors besides boiling point, including redox state of melt, solubility in melt, other metals in melt, flux agents, chemical state when introduced, processing design of melter, and operation of cold cap.

b. Boiling points for most other compounds of the metal than those listed do not exist as the compound decomposes to the metal before the elemental boiling point is reached. Boiling points of exotic salts not expected to be common in the waste such as the iodides and bromides are not listed.

- Low - less than 10% of metals or metal compounds are expected to volatilize
- Medium - up to 40% of metals or metal compounds are expected to volatilize

- High - up to 90% of metals or metal compounds are expected to volatilize

Total Volatilization - greater than 99% of metals or metal compounds are expected to volatilize.

The following conclusions from glass R&D on waste with hazardous metals give rise to the concerns listed below on the ability of glass to stabilize volatile metal species.

1. Glasstech conducted melter tests at 1316°C (2,400°F) to vitrify municipal incinerator flyash contaminated with trace metals. Test observations revealed that most of the heavy or toxic metals exited with the off-gas or remained in the melter head space deposits. Glasstech concluded that the glass captured very little of the metal contaminants. Glasstech attributed the low metal capture to the presence of reducing species such as carbon in the ash. Glasstech anticipates that if the carbon content of the waste was greater than 0.5%, a significant portion of the metals would volatilize and not be captured by the glass.²⁹

2. Babcock and Wilcox Company also conducted melting tests using a cyclone vitrification furnace in which soil containing elemental heavy metals was converted into vitrified slag. Test results indicated that the capture of heavy metals in the vitrified slag was estimated at 8 to 17% for Cd, 24 to 35 % Pb, and 80 to 95 % for Cr. The capture of heavy metals in the slag was inversely dependent on the metal volatility.³⁰

3. EPA conducted tests to determine the fate of metals in high temperature processes. Test results confirm that Cd, Pb, and Bi are relatively volatile metals. According to test data, less than 32% of these metals will remain in the glass product. Feed Cl content had a major effect on the observed volatility of Cd, Pb, and Bi, with volatility increasing with increased feed Cl content. Ba, Ag, Sr, Cr, and Mg are relatively non-volatile, with glass capturing approximately 75% of these metals.³¹

4. Test data from Aptus/EPA high temperature processing indicate that nonvolatile metals such as Cr, Be, and Ni will remain in the high temperature product (more than 95%), while volatile metals such as Ag, Hg, and Pb partition mainly to the combustion gas (more than 80%).

Metals partition to the flue gas by entrainment and by vaporization. Entrainment dominates if the waste is injected as an atomized liquid or as a suspended pulverized solid. However, if the waste is fed to the high temperature vessel as a bulk solid, generally only a fraction of the waste is entrained, and vaporization may be the dominant pathway for metals partitioning to the flue gas. Entrained metals are generally in the form of large particles which are easily removed in off-gas control equipment, whereas vaporized metals condense into or onto very fine particles that are difficult to capture using off-gas equipment. Hence, metals emissions are often dependent on metals vaporization.

5. High temperature processing tests indicate that the presence of chlorine in the feed increases the volatility (and emission rate) of certain metals. The amount of Cl needed for a "maximum" shift in equilibrium of metals toward increased volatility is not certain.³² However, testing has shown that at 0 – 4 wt% chlorine in the waste feed stream metal volatility is significantly increased. Especially for cadmium, lead, and copper, addition of chlorine increased emissions by more than a factor of three.

4.2 HYDRAULIC CEMENT WASTE FORM TEST SUMMARIES

Test results reported here are a sample of those available in existing literature. The tests include work on low-level waste by both DOE contractors and commercial nuclear waste generators, and a small amount of work in recent years on mixed waste. The DOE test results are primarily directed at meeting site specific waste disposal criteria. The commercial tests on reactor waste (radwaste) are directed at meeting NRC position tests to qualify their waste forms. The few mixed waste tests are often directed at different compositions from either the DOE LLMW or commercial radwaste and, therefore, considerably more data are needed to evaluate the potential use of hydraulic cement.

4.2.1 NRC Position Tests

Phillips³³ in 1984, prepared a report that provided excellent guidance to commercial LLW generators on meeting 10 CFR 61 (NRC position) requirements. Westinghouse Hittman used Phillips' guide to test hydraulic cement waste forms for qualification. The tests were generally successful and the cement waste forms were qualified for use with radwaste. Present NRC position test values have been increased for compressive strength from the initial 0.34 MPa (50 psi) to the present 0.41 MPa (60 psi) for all waste forms except cement. The NRC recommends that the present cement waste forms exhibit at least 3.4 MPa (500 psi)³⁴. Building concrete typically exceeds 27.6 MPa (4,000 psi) for 28 day compression strength tests. Cement waste forms generally test less than 27.6 MPa (4,000 psi) but exceed 3.4 MPa (500 psi).

The following sub-sections contain results for all or some portion of the NRC tests by cement-based waste forms.

- Waste salts from the Integral Fast Reactor (IFR) contain a mixture of KCl, LiCl, NaCl, halide fission products, and less than 1 ppm actinides.³⁵ Mortar made from 25% Type I portland cement, 25% Class F fly ash, and 50% blast furnace slag with a water/solids weight ratio of 0.4 had a leachability index of 7 to 9 for the chloride ion and a compressive strength of 40 MPa (5,800 psi) for products with waste loadings to 10%.

The addition of fly ash to the mortars increased set times, offset strength decreases due to inclusion of salt, improved compressive strength, and improved chloride ion

leach resistance. There was also an observed decrease in mortar permeability resulting from slag additions.

- Simulated solid, mostly combustible TRU waste was shredded and grouted with a cement-water paste to form a product termed shred/grout. The waste loading was essentially 100% by volume as the cement paste was mixed into the air voids surrounding the shredded waste. The resulting product was tested after a 28-day air cure. The product passed all of the NRC position tests (in 1987) and other tests. The results are given in Table 4.3.³⁶
- Sauda³⁷ (JGC Corp. of Japan) has developed an advanced cement-solidification for the treatment of radioactive spent ion-exchange resins that meets NRC test requirements. The NRC position test results are summarized in Table 4.4.
- Rosenstiel³⁸ determined that gypsum cement could be qualified to immobilize specific LLW residues as given below:
 - 24% boric acid solutions
 - mixed bed ion exchange bead resin (unexpended)
 - powdered ion exchange resin (unexpended)
 - lubricating oil
 - mixtures of oil and 24% boric acid solution
 - mixtures of mixed bed ion exchange bead resin and 24% boric acid solution
 - mixtures of powdered ion exchange resin and 24% boric acid solution
 - EDTA decontamination fluid
 - a neat aqueous mixture of Envirostone® gypsum cement to simulate encapsulation of solid objects such as used equipment, spent filter cartridges, etc.

4.2.1.1 Compression Strength Emphasis

The basic measurement of the NRC position tests is the compression strength. Measurement of the compression strength is the first major test, and then most of the tests remaining also use compression strength as an indication that the waste form has not lost its integrity. The following literature references address compression strength measurements on cement-based waste forms to provide an indication of strength performance:

- McIsaac³⁹ evaluated decontamination ion-exchange resin wastes and found that compression testing of unleached samples is not indicative of their stability after immersion as some samples disintegrated upon immersion in leachants. Results are given in Table 4.5:
- Place⁴⁰ reports that by destroying the physical structure of the ion-exchange media, its capability to impose significant stresses on the cement matrix was reduced. High shear wet grinding of zeolites and ion-exchange resins improved the compressive

Table 4.3. Results of NRC position test on simulated combustible TRU waste

Test No.	Test Description	Comp. Strength (MPa)	Comp. Strength (psi)	Other Results
1	Compressive Strength	3.52	510	Free standing Monolith
2	Free Liquid	N/A	N/A	None
3	Radiation Stability	1.45, 0.83, 1.10	210, 120, 160	No weight loss No liquid formation
4	Biological Degradation	5.38 (control), 2.90, 3.86, 4.76, 4.48, 6.96	780 (control), 420, 560, 690, 650, 1010	Resists cultures
5	Water Leach	1.45, 5.45	210, 790	Leach index > 10 for iron oxide powder (Pu stand-in)
6	90-day Water Immersion	0.552	> 80	---
7	Thermal Cycling	3.31	480	No degradation
8	Combustion Stability (20 min. Oil Fire Exp.)	---	---	No loss of solid material or integrity
9	Transport Stability (3000 mile transport)	---	---	No free liquid formed nor degradation of solid
10	Forklift tong puncture	---	---	(0.001 wt% of waste dispersed)
11	30-Foot Drop Test	---	---	Drum not breached and no degradation of contents (waste)

strengths of the cemented waste forms. Other pretreatment techniques were also evaluated.

- Shuler⁴¹ determined that the SRL "Ashcrete" (cement immobilization of incinerator ash) achieved compression strengths averaging ≥ 6.89 MPa (1,000 psi) as shown in Table 4.6.
- Stone determined that alumina cement exhibited good compression strengths when used to solidify sludge. Strengths decreased with increased waste loadings. Results are shown below:⁴²

Table 4.4. NRC position test results for radioactive spent ion-exchange resins

No.	Test Item	Test Standard	JGC's Data			
			Spent Bead Resins		Spent Powder Resins	
			18/36/46	20/40/40	18/36/46	20/40/40
1	Compressive Strength (psi)	ASTM C39	1,390±480	1,390±80	3,070±120	1,910±80
2	Radiation Stability (psi)	ASTM C39 (after 10 ⁸ rads)	1,080±10	—	2,550±250	—
3	Biodegradation (psi)	ASTM G21	No growth	—	No growth	—
		ASTM C39	1,440±0	—	2,920±50	—
		ASTM G22	No growth	—	No growth	—
4	Leachability	ASTM C39	1,550±50	—	2,550±550	—
		DW	Co	14.89±0.33	12.58	15.42±0.25
			Cs	7.33±0.02	—	7.12±0.07
			Sr	9.68±0.03	7.80	8.32±0.08
		SW	Co	15.51±0.04	—	15.88±0.19
			Cs	7.37±0.11	—	7.30±0.08
			Sr	9.57±0.18	—	8.53±0.09
5	Immersion (psi)	ASTM C39	1,300±230	330±20	2,650±80	2,000±90
6	Thermal Cycling (psi)	ASTM B 553	1,190±120	—	1,970±10	—
7	Free Liquid	ANS 55.1	0 vol%	—	0 vol%	—
8	Full-Scale Tests (psi)	ASTM C39	1,530±200	—	2,140±130	—
DW: Demineralized water			SW: Sea water			

Tank 5: 65.5 MPa (9,500 psi) at 10% sludge, 62.1 MPa (9,000 psi) at 25% and 20.7 MPa (3,000 psi) at 40%

Tank 13: 62.1 MPa (9,000 psi) at 10% sludge, 48.3 MPa (7,000 psi) at 25% and 11.0 MPa (1,600 psi) at 40%

Tank 15: 46.9 MPa (6,800 psi) at 10% sludge, 33.1 MPa (4,800 psi) at 25% and 9.65 MPa (1,400 psi) at 40%.

Table 4.5. Compressive strengths of waste form specimens

Waste Form	Decontamination Process	Water-to-Cement Ratio ^a	Cure Time (days)	Compressive Strength	
				(kPa)	(psig)
Brunswick-1 cation	Citrox	0.27	486	2.70E+03	392
mixed-bed		0.30	486	3.48E+03	505
FitzPatrick baked	LOMI	0.30	212	1.28E+04	1857
unbaked		0.30	212	1.31E+04	1906
Pilgrim unleached	DOW NS-1	0.37	1705	6.37E+03	924
leached		0.37	— ^b	1.41E+04	2044
Indian Point-3 unleached	LOMI	0.38	1394	6.09E+03	883
leached		0.38	— ^c	1.61E+03	233

a. Ratio of weight of water to weight of cement or slaked lime or sodium hydroxide.

b. The leached waste form specimen was cured for 1.8 years prior to leaching and leached subsequently in deionized water for a total of about 2.1 years.

c. The waste form specimen was cured for 1.5 years before leaching and was subsequently leached in deionized water for a total of 2.1 years. The unleached specimen was cured for 4.7 years before performing the leach test.

4.2.1.2 Leachability Emphasis

Waste form performance assessments depend highly upon leachability results. Leachability and compression strengths are probably the most important aspects of the NRC position tests. The following literature references on leachability or leach index measurements are provided to indicate how cement based waste forms perform:

- Bostick⁴³ demonstrated that beaded anion exchange resins can be incorporated with a moderate (40% by volume) loading into a grout matrix using blast furnace slag with

good waste form integrity. The leachability index for nitrate ion was over 9, and for ^{99}Tc it was 14.

- Mortar with slag was found to decrease the effective diffusivity of Tc and chromium by a large factor over a cement-fly ash mix without slag.⁴⁴ This decrease was attributed partly to the lower permeability and partly to the lower alkalinity and lower oxidizing potential of pore water produced by the slag. Under these conditions, Tc and Cr have a greater tendency to form less soluble compounds.
- Portland cement leach resistance is lower for Cs than other radionuclides because of size and charge considerations. Cs retention has been improved by adding colloidal silica to the cement paste. Most studies have reported an improvement in Cs retention as fly ash, silica fume, clay or zeolites have been added to modify the bulk composition of portland cement. Also, indian red pottery clay has been used in grout formulations⁴⁵ at 8 wt% to ensure intimate contact with ^{137}Cs and its retention by ion-exchange. The addition of limestone flour or microsilica to cement reduces Cs leachability from 45% down to 39% and 16% respectively.⁴⁶ Limestone flour acts as a Cs absorber, and microsilica acts as a pore blocker. Cs leachability performance is also improved by increasing the silica or alumina content of the binding cement matrix.⁴⁷
- Gilliam⁴⁸ determined that slag cement performs better than portland cement for Tc and nitrate leaching, as shown below:

Leach Resistance: 10 to 11 for ^{99}Tc , 7.2 to 7.4 for nitrate (leach indices) for slag cement, 6.1 for ^{99}Tc , and 5.9 for nitrate using Portland Type I-II cement.

Table 4.6. Compression strengths of SRL "ashcrete"

Ash Type	Cure (days)	MPa	psi	Cure (days)	MPa	psi
Solid	7	4.21	610	69	8.96	1,300
Solvent	7	4.14	600	69	14.5	2,100
Baghouse	7	11.0	1,600	69	11.2	1,630
Rubber	6	13.8	2,000	--	--	--
Paper	6	6.67	980	--	--	--
Waste Mix	4	12.2	1,770	--	--	--

- Kalb⁴⁹ determined that general cement radwaste forms tested satisfactory for NRC leachability index (≥ 6) with the exception of cesium leachability for masonry cement over a 99-day interval, as given below:

Leach Index ^{60}Co is 10.1, ^{137}Cs is 5.8, ^{134}Cs is 5.8 for PWR conc. waste in masonry cement.

^{60}Co is 11.6, ^{137}Cs is 6.7, ^{134}Cs is 6.8 for BWR and resin waste in Portland Type III cement.

^{60}Co is 11.8, ^{137}Cs is 6.9, ^{134}Cs is 6.9 for BWR waste in Portland Type III cement.

- McConnell⁵⁰ determined that Three Mile Island (TMI) resin-cement solid (EPICOR II) waste forms containing Cs passed the NRC leach index as given in Table 4.7.

Table 4.7. NRC leach indices for TMI resin-cement solid waste forms

Binder	Waste Type	Radionuclide	Leachant	Index
PC	PF-7	^{134}Cs	DI	10.3
PC	PF-7	^{134}Cs	SW	9.6
PC	PF-7	^{137}Cs	DI	10.1
PC	PF-7	^{137}Cs	SW	9.5
PC	PF-24	^{134}Cs	DI	10.6
PC	PF-24	^{134}Cs	SW	10.4
PC	PF-24	^{137}Cs	DI	10.4
PC	PF-24	^{137}Cs	SW	10.3

DI - deionized water

SW - seawater

- Cowgill⁵¹ determined that leach indices of cement-based waste forms for radwastes varied from 6 to 14 as given in Table 4.8.

Table 4.8. Leach indices of cement-based waste forms for radioactive wastes

Nuclide	Leachability Index
^{137}Cs	6.0 – 10.6
^{90}Sr	7.0 – 10.7
^{60}Co	9.7 – 13.0
^{14}C	12.9 – 14.2
^3H	7.4 – 9.0

- Tallent⁵² determined that leach indices for nitrate and Tc were greater than six for fly ash waste immobilized in slag cement. These results are shown in Table 4.9.

Table 4.9. Nitrate and technetium leach indices for fly ash waste immobilized in slag cement

Nitrate Leach Index	Technetium Leach Index
7.5 for mix	8.2 for mix
7.5 with 7% Indian Red Clay	8.1 with 7% Indian Clay
7.1 with 10% Portland Cement	8.3 with 10% Portland Cement
7.0 with 10% Cement, 7% Indian Clay	8.0 with 10% Cement, 7% Indian Clay

4.2.1.3 Other NRC Position Type Test Results

Other literature references having to do with NRC position tests are given below:

- Gay⁵³ found that chemically spent resins pretreated in a high efficiency dryer are nearly impermeable to water and will not reabsorb and swell when immersed. Spray drying of bead resins produces a virtually dry product of less than 10% absorbed water. Dried resin loadings of up to 28 wt% were tested and passed the immersion test.

4.2.2 EPA Toxicity Characteristic Tests

Mixed wastes that are ignitable, corrosive, or reactive are treated in other facilities such as incinerators, neutralizers, or humidity chambers. The type of mixed wastes covered in this report are those with toxic organic or inorganic chemicals. This subsection addresses EPA type tests and results that have been carried out on cement-based waste forms where toxic materials were immobilized and tests were carried out to verify containment. EPA-type tests and results literature are given below:

- Weitzman⁵⁴ determined that soil could be immobilized and the contents stabilized by use of portland cement, lime, or a lime-fly ash mixture. Representative TCLP results are given in Table 4.10. Favorable test performance was achieved for the EPA-regulated toxic metals As, Cd, and Pb.
- Gilliam⁴⁹ determined that the SRP grout formulation passed the EP toxicity test for 38.3% waste liquid, 11.7% water, 25% portland cement, 25% fly ash composition.
- Langton⁵⁵ also provided specific data on the EPA toxicity test performance of SRP saltstone as given in Table 4.11.

Saltstone is a waste treatment and disposal concept for DOE mixed waste at the SRS. The waste is a sodium salt solution of $8.51\text{E}+06$ Bq/L ($230 \mu\text{Ci/L}$) in addition to the hazardous characteristics of corrosivity ($\text{pH} > 12.5$) and metal toxicity ($\text{Cr}^{+6} > 100$ ppm). The TCLP results for cement-based Saltstone were greatly improved by the addition of slag, and reduction in amounts of cement and fly ash. Saltstone was also developed successfully to dispose of soluble salt wastes containing NaNO_3 , NaOH , NaNO_2 , NaAl(OH)_4 and Na_2SO_4 . Waste loadings for the slag and PCC based saltstone were 46 and 43 wt. % respectively.

- Boehmer⁵⁶ found that up to 12,500 ppm potassium chromate can be immobilized with silicate cement in tests at INEL. The tests show that toxic materials could be immobilized using cement, silicate cement, and Envirostone binders.
- Negatively, EPA⁵⁷ shows an increase in leachability when cement is applied to As-type waste (D004) at high (up to 13%) contamination levels.

4.2.3 Other Tests

Tests, results, or findings regarding the use of cement-based waste forms that are important to the mixed waste treatment issue are given below:

- To better define the range of binder mix proportions,⁵⁸ Westinghouse Hanford Company (WHC) has developed a phase diagram for cement-water waste for single-shell tank waste. This parametric study giving viable composition ranges will be used for cement and polymer-modified cement tests. Similar phase composition

Table 4.10. Representative TCLP results for soil stabilized with Portland cement, lime, or a lime-fly ash mixture

(SARM) Sample No.	Binder (Day)	Arsenic		Cadmium		Chromium		Copper		Lead		Nickel		Zinc	
		a	b	a	b	a	b	a	b	a	b	a	b	a	b
I	RAW	ND		0.53		ND		0.61		0.49		0.27		9.2	
1	PCC(14)	ND		ND	100	0.06	+	0.07	81	0.15	75	0.04	70	0.23	96
14	KD(14)	ND		ND	100	0.06	+	0.04	81	ND	100	ND	100	0.27	94
27	LF(14)	ND		ND	100	0.02	+	0.03	98	ND	100	ND	100	0.14	94
1	PCC(28)	ND		ND	100	0.06	+	0.06	83	0.15	75	0.04	70	0.49	91
15	KD(28)	ND		ND	100	0.09	+	0.03	98	ND	100	ND	100	0.62	73
27	LF(28)	ND		ND	100	0.02	+	0.03	98	ND	100	ND	100	ND	100
II	RAW	ND		0.73		ND		0.89		0.7		0.4		14.6	
4	PCC(14)	ND		ND	100	0.03	+	0.04	92	0.15	82	0.04	83	0.09	99
16	KD(14)	ND		ND	100	0.08	+	0.07	79	0.44	+	ND	100	0.25	97
30	LF(14)	ND		ND	100	ND		ND	100	ND	100	ND	100	0.22	99
4	PCC(28)	ND		ND	100	0.03	+	0.06	89	0.15	83	0.04	83	0.54	94
16	KD(28)	ND		ND	100	0.05	+	0.09	89	0.37	+	ND	100	0.78	89
29	LF(28)	ND		ND	100	ND	-	0.03	90	ND	100	ND	100	0.02	100
III	RAW	6.39		33.1		ND		80.7		19.9		17.5		359	
7	PC(14)	ND	100	ND	100	0.07	+	0.15	100	0.63	95	ND	100	0.58	100
21	KD(14)	ND	100	ND	100	0.22	+	1.02	96	13.3	+	ND	100	4.38	95
33	LF(14)	0.81	52	0.02	100	0.03	+	2.96	87	51	+	ND	100	3.81	96
7	PC(28)	ND	100	ND	100	0.07	+	0.09	100	ND	100	ND	100	0.69	100
21	KD(28)	0.21	98	ND	100	0.12	+	0.85	96	18.3	+	ND	100	4.07	95
33	LF(28)	0.79	51	0.02	100	0.07	+	2.59	87	51	+	0.03	99	3.97	96
IV	RAW	9.58		35.3		0.06		10		70.4		26.8		396	
10	PCC(14)	ND	100	ND	100	0.06	+	0.14	100	0.39	99	ND	100	0.39	100
23	KD(14)	0.16	95	ND	100	0.11	+	1.88	97	12.4	43	ND	100	4.57	97
	LF(14)	1.61	50	ND	100	0.07	+	1.92	96	91.8	+	ND	100	3.22	96
10	PC(28)	ND	100	ND	100	0.06	+	0.17	100	0.37	99	ND	100	0.74	100
23	KD(28)	0.27	92	ND	100	0.12	+	1.67	97	21.4	9	ND	100	3.72	97
	LF(28)	0.98	59	0.02	100	0.07	+	2.18	96	65	+	ND	100	3.64	96
Detection Limits		0.15		0.01		0.01		0.02		0.15		0.04		0.01	

a. TCLP results in ppm.

b. % reduction, corrected for dilution.

ND is the increase over the "unstabilized" (raw) material.

+ - increase over raw SARM.

Table 4.11. EPA test performance of SRP saltstone

	Cement-Based Saltstone		Slag-Based Saltstone	
	EP Toxicity (mg/l)	TCLP (mg/l)	EP Toxicity (mg/l)	TCLP (mg/l)
Ag	< 0.5	< 1	< 0.5	< 1
As	< 0.5	< 0.5	< 0.5	< 0.5
Ba	< 0.5	< 0.5	< 0.05	0.309
Cd	< 0.02	< 0.02	< 0.02	< 0.02
Cr	16	12.5	0.113	< 0.05
Hg	< 0.01	< 0.01	0.00127	0.00566
Pb	< 0.5	< 0.5	< 0.05	< 0.5
Se	< 0.5	< 1	< 0.5	< 1

diagrams predominantly in the system $\text{CaO} - \text{Al}_2\text{O}_3 - \text{SiO}_2 - \text{H}_2\text{O}$ have been investigated⁵⁹ in order to better understand the underlying physical/crystal chemical principles which ultimately govern the leachability of a given ion.

- Organic liquid wastes act as set retardants and they make cement slurries more fluid, thus requiring more portland cement powder. The use of emulsifiers⁶⁰ enabled tributyl phosphate and normal paraffin hydrocarbon LLW to be solidified in cement. Waste loading was increased from 35 vol% to 45 vol% when sodium hydrogen phosphate solution was added to accelerate setting.
- Perry, et al.,⁶¹ reported a high waste-dependent effect of leaching with time on TCLP results for stabilized hazardous waste (cement and other waste forms). However, the report (tables) listed 14 samples that showed little or no change, two samples that showed a substantial increase with time, and one sample whose results looked questionable. Less than 20% (including the questionable result) showed any appreciable time effect. It is not clear whether this is an effect of waste form or merely an effect of quality control when preparing the product.

4.2.4 Conclusions

The conclusions that can be made for hydraulic cements is that in general there are cement-based waste forms that can meet all present applicable disposal criteria, although EPA and some NRC test data are limited. Tests show that cement forms consistently pass NRC-type tests, but have some problem meeting the 90-day immersion test requirements and passing the Cs leach tests for some forms. The use of cement modifiers and additives help in preparing waste forms that do meet NRC and EPA tests.

4.3 SULFUR POLYMER CEMENT WASTE FORM SUMMARIES

Construction data pertinent to evaluation of SPC's potential as a waste stabilization agent are discussed in Section 4.3.1. Tests of SPC as a stabilization agent for hazardous waste, LLW, and mixed waste are summarized in Section 4.3.2. The SPC data offer comparisons with the oldest and most widely used waste stabilization agent, portland cement concrete (PCC).

4.3.1 Sulfur Polymer Cement Tested as a Construction Concrete

The following test data were developed by the U.S. Bureau of Mines and the SPC construction industry, and are pertinent to final waste form analysis and development. For example, if SPC readily accepts rebar, it should, and does, accommodate steel wastes.

SPC's Strengths. Using the same aggregate for both SPC and PCC, SPC has greater mechanical strengths. SPC's mechanical properties depicted in Table 4.12 exist after only one day of cooling.

While Table 4.12 depicts physical and mechanical properties of SPC, there are other qualifying data that further describe SPC's properties:

- SPC achieves its mechanical properties much more quickly than PCC and other hydraulic cements and ultimately gains more overall strength when the same aggregate is used.^{62,63}
- Glass fibers increase the tensile strength and reduce shrinkage.⁶⁴
- SPC resists freeze-thaw damage and has coefficients of expansion compatible with reinforcing steel and PCC.^{65,66}
- Creep is roughly half that of PCC.^{65,66}
- Density is the same for both concretes when the same aggregate is used.⁶⁷
- Viscosity at 135°C (275°F) is 0.025 – 0.050 Pa-s (25 – 50 cp), similar to that of cold engine oil.^{67,68}

Table 4.12. Summary of physical and mechanical properties of Chempruf® (SPC) concrete (after one day)

Compressive Strength (ASTM C 39)	41.4 – 69.0 MPa (6,000 – 10,000 psi)
Tensile Strength (ASTM C 496)	6.2 – 10.3 MPa (900 – 1,500 psi)
Flexural Strength (ASTM C 78)	8.3 – 13.8 MPa (1,200 – 2,000 psi)
Density (ASTM C 642)	2,304 – 2,499 kg/m ³ (144 – 156 lb/ft ³)
Absorption (maximum) (ASTM C 642)	0.10%
Coefficient of Thermal Expansion	11.9 – 15 × 10 ⁻⁶ /°C (6.6 – 8.3 × 10 ⁻⁶ /°F)
Air Content (ASTM C 642)	4 – 8%
Modulus of Elasticity	20.7 – 27.6 × 10 ³ MPa (3 – 4 × 10 ⁶ psi)
Impact Strength Compressive	10 – 15 kg-m (75 – 110 ft-lbs)
Freeze-Thaw Durability (ASTM C 666) [modulus of elasticity retention after 300 cycles (minimum)]	60%

a. *Chempruf Concrete*, October 1988, p. 4-1.

SPC's Qualities in Resisting Destruction. A sampling of reported test results illustrates SPC's resistance to attack by adverse chemicals that routinely attack hydraulic concretes. After being exposed to sulfuric acid solutions and copper electrolytic solutions for nine years, SPC showed no evidence of corrosion or deterioration.⁶⁹ In a six-year test in a chemical processing plant, PCC was attacked and completely destroyed by the chemicals in some cases, while SPC showed practically no evidence of strength loss or material degradation.⁷⁰ After seven years of exposure to a salt environment in a test in a potash chemical storage building, two SPC structural support piers were undamaged, while the PCC pier in the same location was heavily damaged after only two and a half years.⁶⁵ Sulfates attack PCC but have little or no effect on SPC.^{71,67} SPC is a durable, high-strength concrete that is resistant to abrasion and to attack by most acids and salts.^{65,67} However, SPC is not recommended for use in strong alkali (over 10%), strong bases, strong oxidizing agents, aromatic or chlorinated hydrocarbons, or oxygenated solvents.^{67,69}

Temperatures. SPC is a thermoplastic that will always melt in prolonged temperatures $>120^{\circ}\text{C}$ (248°F), and will regain its original strength rapidly when the heat is removed. The recommended mixing temperature for SPC is $130 - 140^{\circ}\text{C}$ ($266 - 284^{\circ}\text{F}$), which will minimize gaseous emissions to the off-gas system and provide optimum viscosity.^{72,73} SPC can be maintained in the recommended pouring-temperature range in a heated mixer for long periods of time, yet remain plastic and workable until placement,^{72,73} or it can be allowed to cool in the mixer and be reheated for the next pour.^{74,72,75} SPC is not menu-dependent like hydraulic cements; when it cools, it solidifies.^{72,76}

Permeability. All water must be removed from the waste prior to mixing with SPC. SPC is inherently less permeable to water than PCC.^{63,67} Tests conducted in the Netherlands and Japan revealed that the addition of Al_2O_3 reduced the porosity of SPC and further improved its impermeability characteristics.⁶³

4.3.2 Sulfur Polymer Cement Tested as a Final Waste Form

BNL, the Netherlands' Energy Research Foundation, state agencies, and the private sector conducted tests of SPC for use in solidification and stabilization of wastes. Many of the tests were conducted with mixed and hazardous wastes.

Waste Loadings. Successful tests included independent loadings ≥ 40 wt% of dehydrated boric acid salts, incinerator hearth ash, LLMW fly ash, and dehydrated sodium sulfate salts.⁷⁶ In meeting EPA and NRC requirements, these combined wastes were loaded with 3.2 times more volume in SPC than in PCC.⁷⁶ These have heretofore defied solidification and stabilization in PCC in any significant quantity.⁷⁶

Toxic Metals. SPC has proven effective in reducing the leach rates of toxic metals to the extent that many MWs can be managed as LLW. When SPC is combined with mercury, cadmium, and lead oxides (all toxic metals), they interact chemically and form metal sulfides that are insoluble in water. Vanadium (a carcinogen), arsenic acid, mercury, iron, and antimony have been microencapsulated in SPC and have passed California EPA and/or U.S. EPA leachability tests.⁷⁷

MW fly ash that contained 37 wt% Zn, 7.5 wt% Pb, 0.2 wt% Cd, and other wastes, such as chloride salts, were added to SPC as a 43 wt% loading and passed the EPA and NRC laboratory tests. It was concluded that radionuclides leach slowly in SPC.⁷⁷

Ion-Exchange Resins. Ion-exchange resins that defied successful loading in SPC in the past were successfully loaded in SPC in a unique procedure developed in the Netherlands. The temperature of the mass was elevated to $220 - 250^{\circ}\text{C}$ ($428 - 482^{\circ}\text{F}$) and held there for three hours in the presence of asbestos or diatomite. The test specimen was immersed in water for one year and showed no signs of deterioration.⁶³ The means of containing or handling the gaseous emissions were not discussed.⁶³

Full-Scale Tests. The NRC's full-scale test has not yet been completed with LLMW and SPC. Successful full-scale test pours of SPC laden with 40 wt% nonradioactive industrial furnace ash were completed in 1-m³ (1.3 yd³) and 0.7-m³ (0.92 yd³) boxes that contained 363 kg (800 lb) of simulated steel waste; the containers and contents were at room temperature. In later tests the ash, disposal box, and simulated steel waste were all preheated. The heat allowed the voids that existed in the previous cold tests to be filled. Also accomplished in these tests were evaluation and modification of the mixer and the procedures required to optimize the pour results. Prototypical rectangular waste containers with no appendages were also tested and modified in these efforts.⁷⁴

Irradiation and Tests for Radiolysis Lead oxide at an 80 wt% loading was combined with SPC and was subjected to 20 MGy (10⁸ rad). It actually gained strength and passed the NRC requirement for 3.4 MPa (500 psi) compressive strength by an order of magnitude. In the search for gas generation, none was detected in the process.⁷⁸ Through optical and electron microscopy, it was determined that SPC and the inorganic waste materials are practically insensitive to radiation. The constituents in hydraulic cements and bitumen that cause radiation effects are not present in SPC.⁶³

Safety Considerations. Airborne SPC dust can be mildly explosive when normal safety precautions are not exercised. SPC will emit H₂S, SO₂, and volatile organic sulfur compounds to the off-gas system if excessive temperatures are allowed [above 160°C (320°F)]; normal heat control systems with backup gas detectors and an appropriate off-gas system will prevent a safety hazard. The addition of Al₂O₃, or Fe₂O₃, essentially eliminates the creation of SO_x.

SPC's flashpoint, as determined by the Cleveland Open Cup method, is 177°C (351°F), and the autoignition is 232 – 254°C (450 – 489°F). [Note: The EPA-required test for ignitability is Pensky-Martin's Closed Cup, Method ASTM D-93.] SPC will burn if held in a flame, but will self-extinguish when the heat is withdrawn.^{61,68} As flame is held on the SPC, a black char develops and is an excellent insulator that causes the SPC to stop burning. The testers in the Netherlands exposed SPC to a gasoline fire for 16 minutes, and only minor surface roughening was observed.⁷⁹ SPC in the solid state meets none of the DOT criteria for classification as a flammable material.^{62,69}

Throughout the world, sulfur is the chemical industry's most widely used raw material; therefore, a great deal of information (all based on tests) is available on handling it safely. Around the world, sulfur is routinely transported in the molten state via train tanker cars and tanker trucks. A safe working environment for both the liquid and solid state is ensured by following the appropriate procedures provided by the National Safety Council,⁸⁰ National Fire Protection Association,⁸¹ U.S. Department of Health and Human Services,⁸² National Institute for Occupational Safety and Health,⁸² and the Manufacturing Chemists' Association, Inc.⁸³ SPC is an alteration of sulfur, and it has even more favorable safety margins than elemental sulfur.

Compression Tests. The Netherlands' scientists combined 23% SPC, 44% sand, and 22% flyash. The increase in compressive strength was fast in the first few hours and days

and continued to increase for months. After one day the compressive strength was 23 MPa (3,336 psi); after 326 days it was 52 MPa (5,652 psi); and after 722 days it was 64 MPa (9,282 psi).⁶³

4.4 CERAMIC WASTE FORM TEST SUMMARIES

There is an extensive body of literature describing the fabrication, characterization, and testing of ceramic waste forms for high level and TRU wastes. Review articles were published in 1988⁸⁴ for SYNROC, tailored ceramics, TiO_2 ceramic matrix, glass-ceramics, and monazite. The review articles contain extensive bibliographies and provide a comprehensive review of the literature for those waste forms for literature published prior to 1987. The material that follows is drawn from those review articles and from the references contained therein. Studies conducted within the last five years have added to the database contained in the review articles, but have not altered the basic conclusions contained in the review articles. Recent work on new ceramic waste forms has been reported in conference proceedings⁸⁵ and in the proceedings volumes for the Materials Research Society (MRS) symposia conducted in prior years. The literature on chemically-bonded ceramics, such as AlPO_4 , ZrPO_4 , and $\text{Mg}(\text{NH}_4)\text{PO}_4$, for waste incorporation is less extensive. AlPO_4 with single-phase berlinite has been developed and tested for simulated ICPP waste.⁸⁶ The pressure and temperature conditions have been identified to synthesize this waste.

The specific properties of a ceramic waste form depend on the particular mineral phases of which it is composed. These phases are selected by the waste form designer to accommodate the chemical species present in the particular waste stream, to be compatible with each other, and to be chemically durable in the disposal environment. It is therefore not possible to specify exact property values *a priori* for a generic ceramic waste form that will accommodate any unspecified waste stream. Consequently, the following data should be viewed as applying to particular examples, not as representing a ceramic waste form for any arbitrarily chosen waste stream.

SYNROC-C⁸⁷

SYNROC-C is a fine-grained, polyphase crystalline ceramic composed primarily of the minerals hollandite, zirconolite, perovskite, and titanium oxides and/or minor calcium-aluminum titanates, plus small amounts of metallic alloys and a calcium-rich phosphate. Results of tests conducted on SYNROC-C are summarized in Table 4.13.

SYNROC-D⁸⁸

SYNROC-D is a fine-grained, polyphase ceramic composed of the minerals zirconolite, perovskite, spinel, and nepheline, and a silicate glass phase. A summary of test results for SYNROC-D is presented in Table 4.14.

Tailored Ceramic RSC-S29⁸⁹

The tailored ceramic RSC-S29 is described as a fine-grained, polyphase crystalline ceramic composed primarily of the minerals nepheline, spinel, zirconolite, perovskite, murataite, magnetoplumbite, and an amorphous phase. Test results for the tailored ceramic RSC-S29 are provided in Table 4.15.

Table 4.13. SYNROC-C

Waste type treated	High-level waste from reprocessing of power reactor fuel.
Waste volume change	Depends on original density of waste stream. The density of SYNROC-C is 4.35 g/cm ³ (1.57E-07 lb/in ³), and the waste loading is ≤ 20 wt %.
Development status	10 kg/hr non-radioactive demonstration plant operated in Australia. Over 2,500 kg (2-1/2 tonnes) have been processed. Radioactive samples made in England. Full scale plant in planning stage in Australia.
Compressive strength	574 MPa (83,300 psi)
Resistance to thermal cycling	Not reported. SYNROC-C is hot-pressed at 1,180°C (2,156 °F) and cooled. Thermal conductivity is 2.1 W/m-K. Thermal expansion coefficient is $10.5 \times 10^{-6} \text{ K}^{-1}$. Young's Modulus is 2.0E+05 MPa (2.9E+05 psi). Tensile strength is 56 MPa (8,100 psi).
Biological stability	Not tested. SYNROC-C minerals found in nature are more than 500 million years old.
Immersion	No short-term effects observed.
Free liquid	None [fired at 1,180°C (2,156 °F)].
Chemical stability	Extremely stable. Perovskite and zirconolite samples found in nature with ages of 500 million years and more.
Compositional flexibility	Can accommodate from 5 to 22 wt% high level waste without serious effect on leach rates. Addition of Na and Si at levels of the order of 1 wt% increases Cs leach rate by an order of magnitude or more. 1 wt% P ₂ O ₅ addition doubles Sr leach rate.
Gas generation	None reported. High-fired ceramic.
LDR Compliance	Not ignitable, corrosive, or reactive. Not tested using TCLP.
Solubility	SYNROC-C is believed to form a TiO ₂ protective layer on the titanate minerals in contact with water. The solubility of TiO ₂ is about 3 orders of magnitude less than that of SiO ₂ .

Table 4.14. SYNROC-D

Waste type treated	SRS composite high level defense waste sludges.
Waste loading	60 to 65 wt.%, with a product density of 3.85 – 4.0 g/cm ³ (1.39E-01 – 1.45E-01 lb/in ³).
Development status	Pilot scale (non-radioactive) processing demonstrated up to 100 kg/day (2.20 lb/day). Hot isostatic pressing (nonradioactive) demonstrated at sizes up to 50 kg (110 lbs).
Compressive strength	279 MPa (4.05 x 10 ⁴ psi)
Resistance to thermal cycling	Not reported. SYNROC-D is hot-pressed at 1,050 – 1,100°C (1,922 – 2,012°F) and cooled. Thermal conductivity is 1.85 (W/m-K). Thermal expansion coefficient is 10 x 10 ⁻⁶ K ⁻¹ . Young's modulus is 1.03E+05 MPa (1.50 x 10 ⁷ psi). The tensile strength was not measured, but the hardness values were about 15–20% lower than for SYNROC-C.
Biological stability	Not tested. Main radionuclide-containing phases occur as natural materials, 500 million years old.
Immersion	No short-term effects observed.
Free liquid	None [fired at 1,050-1,100°C (1,922 – 2,012°F)].
Chemical stability	Extremely stable. Perovskite and zirconolite samples found in nature with ages of 500 million years and more.
Compositional flexibility	Batches were prepared for waste stream compositions spanning wide ranges, e.g., Fe ₂ O ₃ : 5.3 to 53 wt%, Al ₂ O ₃ : 4.89 to 76 wt%, U ₃ O ₈ : 1.3 to 12 wt%. Flexibility of waste stream composition for a single recipe of additives was not studied in detail.
Gas generation	Not reported. High-fired ceramic.
LDR Compliance	Not ignitable, corrosive, or reactive. Not tested using TCLP.
Solubility	Titanate minerals are believed to form a TiO ₂ protective layer in contact with water. The solubility of TiO ₂ is very low, about 3 orders of magnitude lower than that of SiO ₂ . Dissolution of the nepheline and silicate glass is dominated by solubility of SiO ₂ in water, which has an effective value of about 10 ⁻⁴ moles/liter in "equilibrium" with vitreous SiO ₂ at pH 7 and 250°C (482°F).

Table 4.15. Tailored ceramic RSC-S29

Waste type treated	SRS composite high level defense waste.
Waste loading	60 wt %, density-3.97 g/cm ³ (1.43E-01 lb/in. ³).
Development status	Uses similar technology to SYNROC-D. Not completely optimized.
Compressive strength	Not reported, but should be similar to SYNROC-D.
Resistance to thermal cycling	Not reported. Hot isostatically pressed at 1,040°C (1,904°F) and cooled.
Biological stability	Not tested.
Immersion	No short term effects expected.
Free liquid	None [fired at 1,040°C (1,904°F)].
Chemical stability	Extremely stable. Perovskite, zirconolite, and magnetoplumbite are found in nature with great ages.
Compositional flexibility	Not studied in detail.
Gas generation	Not expected.
LDR compliance	Not ignitable, corrosive, or reactive. Not tested using TCLP.
Solubility	(see SYNROC-D).

Leach resistance of ceramic waste forms

The leach resistance of ceramic waste forms depends on the particular minerals that incorporate the radionuclides. Zirconolite, perovskite, and magnetoplumbite are highly leach resistant. The glass phases behave similarly to glass waste forms in terms of leaching, being more leachable than the crystalline phases. RSC-S29 has less of a glass phase than SYNROC-D, and is therefore more leach-resistant.

SYNROC-C and SYNROC-D have been tested for chemical durability using a wide variety of procedures and leaching solutions. Static MCC-1 and MCC-3 type tests have been done with deionized water, silicate solution, and salt solutions. Semi-static testing using the International Atomic Energy Agency (IAEA) test procedure, or a modification of that procedure allowing less frequent changes of leachate, have been done using deionized water, salt solution, and silicate-bearing groundwater. Flow-through tests at low and high flow rates have also been done. Samples prepared by hot isostatic pressing and by sintering have been tested in static and semi-static leach tests and give comparable results. Data on the leach resistance of SYNROC-C were summarized by Oversby⁹⁰ and by Ringwood.⁸⁷ Samples have been tested at temperatures ranging from 25°C – 200°C (77 – 392°F). Leach resistance was excellent at all temperatures.

The leaching tests on ICPP simulated chemically-bonded ceramic waste forms performed by Sliva and Sheetz⁸⁶ demonstrate good leaching performance for Cs and Sr over the pH range of 3 to 11.

Radiation stability for ceramic waste forms

The identity and quantities of radionuclides present in a waste form determine the type and amount of radiation to which it will be subjected during long term storage. If the radionuclides are beta and gamma emitters, the radiation effect will primarily be ionization of electrons. If alpha emitters such as Pu are to be incorporated, atomic displacements must be taken into account.

Generally speaking, beta and gamma radiation which produce ionization have little effect on the structural or leaching properties of titanates and aluminates, while silicate-based systems may have some sensitivity. Alpha radiation at high doses can cause some swelling of ceramic materials, and some are subject to metamictization (conversion to an amorphous structure, similar to glass) at very high doses.

In comparison with classes of solid materials such as alkali halides or polymers, ceramics are much more radiation-resistant, ranking with metals and glasses. To be more specific about the radiation stability of ceramics, it is necessary to specify the particular ceramic and type and amount of radiation of concern.

4.5 ORGANIC BINDER TEST SUMMARIES

This section summarizes the results of tests of the organic binders. Thermoplastic binders such as bitumen and polyethylene, and thermosets such as polyesters (vinyl ester styrene), epoxies, and UF are covered.

4.5.1. Bitumen

Waste Form Types and Loadings. Because bitumenization of waste is a mechanical rather than a chemical process, most waste types can be successfully solidified with bitumen. The major exception is oil. Oil tends to emulsify bitumen, and should be limited to less than 1% of the feed stream.⁹¹ Other waste types will become bitumenized waste forms with a success that depends on the waste-to-binder ratio. In general, the higher the waste loading, the less durable the waste form. Waste loadings up to about 40% may be acceptable.

Compressive Strength. The most common test method for measuring compressive strength of bituminous waste forms is ASTM D-1074. The compressive strength for bituminous waste forms is generally relatively low compared to other waste forms, with recorded results ranging from about 0.34 – 8.3 MPa (50 – 1,200 psi).^{92,93} Bitumen is not a true solid, but a viscoelastic material, and may creep over time. The NRC recommends control of backfill material used in disposal to ensure minimization of trench subsidence.

When immersed for 90 days in deionized water or simulated seawater, bitumen waste forms containing certain waste streams sometime swell and may eventually disintegrate. This is mainly true of ion exchange resins, although decreased waste loadings or pretreatment of the resins may minimize or prevent this effect.^{94,92,95}

Leaching Resistance. As a water-resistant material, bitumen's true strengths are reflected in its low leachability. The LI (measured in accordance with ANS/ANSI 16.1) tends to be about 8 or greater and can range as high as 14.^{92,96,97,98} No information was found on bituminous waste form performance under the EPA's TCLP, but when samples are subjected to the EP Toxicity test, the leachate concentrations of eight toxic metals in the samples were near the lower limit of detection.⁹⁷ One exception to the generally good leaching properties of bitumen was reported by Swindlehurst,⁹⁹ who found that for a sodium-based waste, chlorine did not pass the ANS 16.1 leach test. For an arsenic sulfide waste, asphalt binder was shown to reduce leachability of As from 41 – 1.7 mg/L.⁵⁷ Similar results have been reported for As-containing by-product salts when encapsulated with asphalt.⁵⁷

Radiation Stability. Irradiation testing may also cause slumping or shape change if samples are unconfined, but this is a problem only with regard to subsequent compressive strength testing. In addition, irradiation testing [which involves exposure to 10^6 Gy (10^8 rad)] is generally performed at high dose rates which are not representative of actual expected conditions. This is important to consider because a high dose rate [$>10^4$ Gy/hr ($>10^6$ rad/hr)] may lead to swelling from hydrogen gas generation at a higher rate than can diffuse from the sample.

Thermal Stability. Thermal cycling of bituminous waste forms (in accordance with ASTM B553) has little effect on the material integrity. Bitumen may crack at low temperatures, but as a thermoplastic material it tends to be self-healing as the temperature rises. If samples are unconfined during testing, they may slump or otherwise change shape. This is not representative of real-life applications where the material is likely to be cast in 0.24 m³ (55-gal) drums or other containers, and is only a problem with regard to subsequent laboratory compressive strength testing, which requires cylindrical samples. Typically, laboratory specimens have been wrapped in foil to maintain the specimen shape throughout the temperature cycles. The foil may be then removed or left in place after cooling to compression-test temperature.

Biodegradation. Biodegradation of bituminous waste forms has little or no effect on the material.^{100,91,101,98} Exposure to fungi and bacteria in accordance with ASTM G-21 and G-22 resulted in some instances of growth, but testing by the Bartha-Pramer Method shows that any biodegradation is negligible. Microbes specified by ASTM G-21 and G-22 are not preferential to bitumen. Other microbes with more affinity for bitumen have been investigated and this research (predominantly Canadian) also indicates that degradation rates are relatively low.¹⁰⁰

4.5.2 Polyethylene

Waste Form Types and Loadings. Polyethylene has been successfully incorporated with nitrate wastes from both the Rocky Flats Plant (RFP) and SRS.¹⁰² Waste loadings of nitrates have ranged from 5 to 70 wt%. Simulated waste types that have been treated with polyethylene are BWR evaporator concentrates (sodium sulfate), PWR evaporator concentrates (borates), incinerator ash, and ion exchange resins with loadings ranging from 30 – 70 wt%.^{102,103,104,105} In most of the studies, commercially manufactured (Gulf Oil Co. and Eastman Chemicals, Inc.) low-density polyethylene (LDPE) was used as the solidification agent.

Compressive Strength. Compressive strengths of various polyethylene waste forms, along with their waste contents and test methods, are summarized in Table 4.16.^{102,106,107}

Table 4.16. Summary of compressive strengths of polyethylene waste forms

WASTE TYPE	WASTE LOADING (wt%)	TEST METHOD	STRENGTH (MPa)	STRENGTH (psi)
Sodium nitrate salt waste (RFP)	30-70	ASTM D-695	0.048 – 17	1,000 – 2,500
Dried sodium sulfate	40-70	ASTM D-695	0.13 – 32	1,943 – 4,650
Ion exchange resins	40-60	ASTM D-256	22	3,300

After 90 day water immersion tests, conducted on various loadings of sodium nitrate salt waste loaded (30 – 70 wt%) in polyethylene, there was no significant reduction in compressive strength observed. Furthermore, after water immersion tests for 70 wt% waste loading, NRC strength criterion was exceeded by an order of magnitude [≈ 0.028 MPa (≈ 600 psi)].¹⁰²

Leaching Resistance. Table 4.17 lists the range of leachability of various elements from polyethylene waste forms following the ANS 16.1 Leach Test.^{102,104,108} Leachability indices for all of the radionuclides satisfy the NRC criterion of >6 .

TCLP and EP Toxicity characterizations have been conducted on polyethylene loaded with 60 wt% sodium nitrate (RFP) to evaluate leaching characteristics of hazardous constituents.¹⁰² Some of the criteria metals, such as Cr, Cd, Pb, and Ba, showed concentrations well within the EPA allowable limits. Results of EP Toxicity and TCLP testing for sodium nitrate-loaded polyethylene waste forms are shown in Table 4.18.

Table 4.17. Summary of leachability indices for polyethylene waste forms

WASTE TYPE	WASTE LOADING (wt%)	RADIONUCLIDE	LEACHABILITY INDEX
Sodium Sulfate	10 – 50	⁶⁰ Co	11.5 – 10.1
		⁸⁵ Sr	13.9 – 10.2
		¹³⁷ Cs	14.7 – 9.9
Incinerator ash	25 – 35	⁶⁰ Co	13.9 – 12.7
		⁸⁵ Sr	15.5 – 14.9
		¹³⁷ Cs	12.5 – 11.3
Ion exchange resin	10 – 30	⁶⁰ Co	13.6 – 14.6
		⁸⁵ Sr	16.2 – 16.1
		¹³⁷ Cs	18.2 – 19.5
Sodium nitrate	30 – 70	Na	11.1 – 7.8

Table 4.18. Results of EP toxicity and TCLP for sodium nitrate (RFP) loaded polyethylene waste form¹⁰²

WASTE FORM AND TEST	Cr (ppm)	Cd (ppm)	Pb (ppm)	Ba (ppm)
60 wt% RFP salt in polyethylene (TCLP)	3.6	0.2	0.3	<0.5
60 wt% RFP salt in polyethylene (EP Toxicity)	0.8	0.1	0.2	<0.5
EPA Allowable Limits	5.0	1.0	5.0	100

Radiation Stability. Exposure of polyethylene to radiation can lead to several changes in properties because of increased cross-linking or bond scission of the polymer.¹⁰² These changes affect thermal stability, permeability, stress cracking, and impact resistance of polyethylene.¹⁰⁹ Tests at Oak Ridge National Laboratory (ORNL)

have shown that a dose of 10^4 Gy (10^6 rad) of ^{60}Co does not damage the polymer. However, large doses can lead to shrinkage. Waste forms containing 50 – 60 wt% ion-exchange resins showed a drop in strength from 29.0 – 19.1 MPa (4,200 – 2,770 psi) after being irradiated to a dose of 10^6 Gy (10^8 rad).¹¹⁰ However, this observation has not been corroborated by other experimental data and is contrary to other experimental evidence and theoretical predictions.¹¹¹ Depending on the dosage and irradiation source, evolution of gases such as hydrogen, methane, ethane, and other hydrocarbons can occur.^{112,113} Estimates ranging from $4\text{E-}06$ – $4\text{E-}02$ L/day have been made for hydrogen evolution because of self-irradiation from 0.24-m^3 (55-gal) polyethylene waste forms containing 60 wt% sodium nitrate wastes from BWRs.¹⁰² Pilot-scale sodium nitrate waste form specimens, on being exposed to ^{60}Co gamma radiation at a dose rate of $3.6\text{E+}04$ Gy/hr ($3.6\text{E+}06$ rad/hr) for a total dose of 10^6 Gy (10^8 rad), increased in compressive strength compared to unirradiated specimens. Moreover, various polyethylene waste forms containing simulated wastes such as sodium sulfates, borates, incinerator ash, and ion exchange resins do not show any significant degradation in compressive strength after exposure to dosages as high as 10^6 Gy (10^8 rad), thus satisfying NRC guidelines.¹¹⁴

Thermal Stability. Polyethylene waste forms have been subjected to thermal cycling in accordance with the procedures outlined in ASTM B-553 to evaluate their durability with respect to temperature variations. In most cases, compressive strengths have been evaluated after thermal cycling by following the ASTM D-1074 procedure.¹⁰⁴ Simulated waste forms, with a wide range of loadings with various wastes such as sodium nitrate, sodium sulfate, incinerator ash, and ion exchange resins, exhibit minimal strength degradation after thermal cycling and satisfy the minimum strength criterion set by NRC.^{102,114,115,106,107}

Polyethylene waste forms are flammable, especially those that encapsulate strong oxidizing agents such as nitrate salts. Polyethylene was rated at 1 on a scale of 0 (least flammable) to 4 (most flammable). Under the ASTM D-1929 test procedure, flammability of polyethylene containing various loadings of sodium nitrate and sodium nitrite salts have been conducted.¹⁰² Other researchers have studied ignitability of polyethylene waste forms.^{116,117} Ignition temperatures are lowered from 465°C (869°F) for pure polyethylene to 365°C (689°F) for polyethylene loaded with 50 wt% nitrate salt waste from the SRS. However, tests conducted at BNL have shown that the sodium nitrate salt wastes from the RFP, encapsulated in polyethylene, do not burn violently and that the waste form is not classified as an oxidizer by the DOT.¹⁰²

Biodegradation. Polyethylene waste forms containing sodium sulfate, boric acid, incinerator ash, and ion-exchange resins are not susceptible to biodegradation.¹⁰⁴ Testing of sodium-nitrate-loaded polyethylene waste forms was conducted in accordance with ASTM G-21 and G-22 to evaluate the attack of fungi and bacteria on the waste form. No growth was observed, although a slight decrease in compressive strength was attributed to solubilization of nitrates in the solvents used for conducting the biodegradation tests.¹⁰² Similarly, for other waste types (Na_2SO_4 , borates, incinerator ash, and ion-exchange

resins), compressive strength after biodegradation testing did show some drop, but in all cases, the NRC minimum criteria of 0.41 MPa (60 psi) is satisfied.¹¹⁴

4.5.3 Vinyl Ester Styrene

Waste Form Types and Loadings. Vinyl ester styrene has been used for containment of various wastes including BWR and PWR evaporator concentrates, ion exchange resins, decontamination wastes, volume-reduced dry salts, and incinerator ash.^{114,118,119} Moreover, it has been demonstrated that vinyl ester styrene can be used for solidifying wastes such as nitrate salts, soils, sludges, oily wastes, Zircaloy cladding, and waste streams containing as high as 10% trichloroethylene. Extremely high loadings for both solid and aqueous wastes can be achieved with this polymer. Waste to binder ratios of 2:1 by volume have been achieved.¹¹⁴

Compressive Strength. Compressive strengths for vinyl ester styrene waste forms are relatively high compared to those of most organic binders and meet NRC structural integrity requirements. Typical strengths have ranged from ≈ 11.7 MPa ($\approx 1,700$ psi) for BWR wastes to ≈ 51.7 MPa ($\approx 7,500$ psi) for dry salts and incinerator ash wastes. Compressive strengths measured in vinyl ester styrene waste forms loaded with a range of waste types showed no significant strength degradation after immersion in deionized water for 90 days, thus exhibiting superior long-term water-immersion integrity.^{114,120}

Leaching Resistance. Leaching resistance of the vinyl ester styrene waste form normally satisfies NRC allowable limits. Leaching indices for ^{60}Co and ^{137}Cs obtained from the ANS 16.1 leach test for vinyl ester styrene waste forms conducted at Dow Chemical and BNL are summarized in Table 4.19.¹¹⁴

Prior heating of the waste form results in increased leachability.¹²¹ Release of organic reagents from vinyl ester styrene waste forms containing decontamination resins has been found to be lower than that for cement waste forms.¹²⁰

Radiation Stability. Vinyl ester styrene waste forms are fairly stable with regard to radiation effects. Compressive strength measurements of various vinyl ester styrene waste forms, made after irradiation with 10^6 Gy (10^8 rad) dose, show no reduction in strength. Moreover, in certain cases there is a slight increase in strength, which may be due to increased cross-linking of the polymer.¹²² In some vinyl ester styrene waste forms, exposure to high doses of radiation [$>6\text{E}+06$ Gy ($>6\text{E}+08$ rad)] has led to higher leachability rates.¹²³

Thermal Stability. ASTM B-553 tests conducted to evaluate the effects of thermal cycling on the strength of vinyl ester styrene waste forms show some drop in strength, but show high enough strength to satisfy the NRC criterion.¹¹⁴ Vinyl ester styrene waste forms have been found to char and lose weight on exposure to burning fuel oil, but they do not sustain combustion.¹²⁴ The process for making vinyl ester styrene is extremely flammable and requires extensive fire controls.¹¹⁸

Table 4.19. Summary of leachability indices for various vinyl ester styrene waste forms

WASTE TYPE	WASTE:BINDER VOLUME RATIO	^{60}Co	^{137}Cs
BWR concentrate	1.5	10.5	10.9
PWR concentrate	1.65	10.4	10.9
Ion exchange bead resin	2.0	17.1	16.3
Powdered ion exchange resin	2.0	12.0	13.2
Filter aid sludges	1.5	9.2	9.3

Biodegradation. Biodegradation testing (ASTM G-21 and G-22) for both fungal and bacterial resistance of vinyl ester styrene waste forms shows that there is no effect on the material.¹¹⁴

4.5.4 Epoxy

Waste Form Types and Loadings. Waste streams that have been treated by epoxies include dry sodium borate, wet ion exchange resins, and Magnox fuel element debris.^{125,126} Epoxies have been used to stabilize fly ash waste generated at the Scientific Ecology Group (SEG) incinerator in Oak Ridge, Tennessee.¹¹⁸ SEG reports indicate that the waste loading in the epoxy waste form is 35 – 40 wt%.

Compressive Strength. The reported compressive strength of epoxies with sodium borate powder is as high as 110 MPa (16,000 psi).¹²⁵ On the other hand, with Magnox debris, compressive strength decreases to about 20.7 MPa (3,000 psi).¹²⁶ SEG has reported that epoxy wastes with incinerator fly ash satisfy the NRC mechanical integrity criterion for both the as-formed waste form and after water immersion testing.

Leaching Resistance. Epoxies loaded with 70 wt% dry sodium sulfate wastes showed leachability of less than 1% over a period of seven days.¹²⁷ Based on an IAEA leach test, leaching characteristics of ^{54}Mn , ^{60}Co , and ^{137}Cs were determined in epoxies loaded with dry sodium borate and wet ion-exchange resins.¹²⁸ Table 4.20 lists the various leaching rates. For comparison, the leaching rates of ^{59}Fe and ^{137}Cs from Magnox wastes were about 10^{-7} cm/d (3.9E-07 in./d) and 1.2E-05 cm/d (4.7E-06 in./d), respectively. For SEG flyash, leaching of heavy metals such as Pb is a problem because of the high concentration of metals in the waste.¹¹⁸ TCLP leaching results have indicated that if toxic

metals are not treated with proprietary additives to form insoluble species, toxic metal concentration in the leachates will exceed EPA allowable limits.

Table 4.20. Leachability rates for various radionuclides from epoxy waste forms¹¹⁴

RADIONUCLIDE	SODIUM BORATE WASTE		ION EXCHANGE RESIN WASTE	
	(cm/d)	(in./d)	(cm/d)	(in./d)
⁵⁴ Mn	5.75E-06	1.46E-05	2.02E-05	7.95E-06
⁶⁰ Co	4.61E-04	1.81E-04	8.85E-05	3.48E-05
¹³⁷ Cs	1.14E-06	4.49E-07	4.58E-04	1.80E-04

Radiation Stability. Tests conducted at the Nuclear Research Center of Grenoble, France have shown release of CO₂, H₂, CH₄, and other organics from various epoxy waste forms containing embedded concentrates, ion exchange resins, and sludges when irradiated with 5E+07 Gy (5E+09 rad) of ⁶⁰Co gamma rays.¹¹⁴

Thermal Stability. Epoxy waste forms are nonflammable and have self-extinguishing properties.^{114,122} Flammability tests conducted on full-scale waste forms at temperatures higher than 800°C (1,472°F) for 40 minutes did not ignite the waste form. ASTM D-635-68 tests conducted on epoxies showed them to be self-extinguishing. Similar observations have been made for epoxy waste forms containing 70 wt% dry sodium sulfate salts.¹²⁷ Exposure to flame for three minutes resulted in smoldering of the material and self-extinguishing within one minute.

Biodegradation. No information was found in the references reviewed regarding biodegradation characteristics of epoxy waste forms.

4.5.5 Urea-Formaldehyde

UF is not commonly used as a solidifying agent because of the numerous problems encountered with the generation of corrosive free liquids.

Waste Form Types and Loadings. Urea-formaldehyde has been used to incorporate spent ion exchange resins, borates, dewatered filter sludges, and sulfate wastes, with waste loadings as high as 25 wt%.^{114,122}

Compressive Strength. Compressive strengths of UF are relatively low compared to those of other waste forms and depend on the waste/binder ratio. Typical compressive

strengths range from about 0.42 – 2.67 MPa (61 – 387 psi) for a range of reactor waste types.¹²⁹ UF with no waste additions has a compressive strength of about 4.83 MPa (700 psi). It has also been observed that prolonged drying can result in lower strengths.¹³⁰

Leaching Resistance. Leaching rates of ^{60}Co , ^{85}Sr , and ^{137}Cs from UF waste forms are generally higher than those of other waste forms and are reported to be about $10^{-1} - 10^{-2}$ g/cm²-d (2.05 – 0.205 lb/ft²-d).^{131,113} Leaching characteristics depend on the type of leachant, i.e., distilled water, salt water, or tap water. It has been found that gamma-irradiation at doses greater than 10^6 rad can lead to increased leachabilities of ^{137}Cs and ^{85}Sr .¹³²

Radiation Stability. Doses of more than $3\text{E}+04$ Gy ($3\text{E}+06$ rad) cause mild to moderate damage, but doses above $2\text{E}+05$ Gy ($2\text{E}+07$ rad) can result in severe damage.¹³³ Problems such as release of radiolytic gases and swelling of the polymer, etc., can occur upon excessive radiation exposure.

Thermal Stability. Urea formaldehyde waste forms burn on exposure to flame but are also self-extinguishing. On burning, the free water at the surface of the UF waste form evaporates, resulting in a charred and insulating surface. The large weight losses observed in UF waste forms are due to evaporation of free water.

Biodegradation. The biodegradation properties of UF have not been extensively characterized and documented in literature. While it is reportedly susceptible to biodegradation,¹³⁴ this is questionable because the pH of the waste form is 1.5 – 3.0 and microbes are not active in acid environments.¹¹⁴

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5. ADVANTAGES AND DISADVANTAGES FOR WASTE FORMS

5.1 GLASS WASTE FORMS

Numerous glass waste forms, in particular the borosilicate high-level waste glasses, have been extensively tested and characterized over the last twenty to thirty years. Laboratories and universities have studied the properties of these glasses under various types of repository conditions. Current research around the world favors the use of borosilicate glass to immobilize high level waste from defense and reprocessing of commercial fuel. More recently, glass has been considered as a waste form for hazardous and mixed waste.

Glass properties are primarily dependent on glass composition, and since silica makes up the majority of the composition for most silicate glasses, many such glasses have properties which are quite similar. For example, the Young's Modulus of Elasticity for most silicate glasses falls between $5.5\text{E}+04$ and $8.27\text{E}+04$ MPa (8 and 12 million psi). In addition, unlike many other waste forms, the properties of glass are not dependent on the raw materials selected for the glass composition; only the oxide composition is critical. As an example, the Al_2O_3 present in soil composed of clay and reagent grade Al_2O_3 would behave exactly the same when vitrified into glasses of the same final oxide composition. For these reasons, much of the knowledge already obtained for commercial glasses and high-level waste glass may be applicable to mixed and low level waste forms.

5.1.1 Advantages of Glass Waste Forms

The advantages of using glass as a final waste form include the following:

- No free liquids
- Chemical durability
- Biological durability
- Compositional flexibility
- Leach resistance
- Compressive strength
- Physical durability.

No Free Liquids. Because vitrification is usually carried out at temperatures in excess of $1,000^\circ\text{C}$ ($1,832^\circ\text{F}$), there are no free liquids.^{1,2,3} Certain vitrification processes may increase the thermal destruction of hazardous organics by pyrolysis and combustion or the liquids may volatilize into the offgas system.

Chemical Durability. Glass is inert and does not readily interact with chemicals other than hydrofluoric acid. Interaction with water and other specific chemicals is described in detail under the section on leach resistance.

Biological Durability. The glass waste form is not influenced by biologic activity.

Compositional Flexibility. Glasses can accept a wide range of chemical elements into the glass network. This permits the solidification of variable waste streams at high waste loading levels. Glass is characterized by a random network structure which is open on an atomic basis and can incorporate into the structure many additional oxides. At least small amounts of nearly all the chemical elements are "soluble" in glass. This includes radiolytically produced gases such as radon, which are maintained in the open network. Waste streams which have the most potential for vitrification include the following:

- Aqueous, acidic, or basic liquids, sludges, filter cake or residue composed largely of metal hydroxides, carbonates, nitrates, or silicates including toxic metal compounds
- Ion exchange zeolites or inorganic filtration media
- Most inorganic solids, including absorbent solids, ash, cemented sludges, soils, dusts, and particulates
- Asbestos-containing materials, glass fiber filters, glass and ceramic particles.

Leach Resistance. The leach resistance of a waste form is one of its most important properties. Leach resistance provides a measure of how well the waste form will resist chemical solution attack and retain the immobilized radionuclides or hazardous materials when exposed. While many waste forms have good initial leach resistance, this property can deteriorate with time. It has been shown that vitrification produces a product in which the leaching reduces over time.

An advantage of glass is that the waste form can be homogeneous on an atomic scale and the leach process occurs only at the glass-water interface. Glass waste forms possess good leach resistance under high-level repository-related conditions; the leach resistance of the glass generally improves with time.⁴ This improvement can be attributed to solution saturation⁵ and the beneficial effects of protective surface layers that can form on the glass during leaching. Because glass can be cast into large monoliths and leaching is dependent on surface interaction, the size of the waste form can be an advantage for stability. The EPA considers vitrification as the BDAT to achieve low levels of leaching of arsenic.⁶

Compressive Strength. Glasses tested at temperatures below the transition temperature [450 – 500°C (842 – 932°F)] have compressive strengths approaching the level of geologic formations. When glass fails or cracks it is due to tensile stress at a pre-existing flaw. Cracking and failure of the glass form is generally due to stresses encountered during the cooling of the glass form or to impact during handling. The surface area of the glass waste form may increase by about five times as a result.⁷

Physical Durability. The glass waste forms have long-term physical durability. At temperatures below the transition temperature [approximately 450 – 500°C (842 –

932°F)] the glass is immune to crystallization or other phase transformations. The material is essentially biologically inert, contains no free liquids, and does not react with air or chemicals other than those mentioned previously. Glass has been shown to be capable of withstanding a dose equivalent to self irradiation from the radionuclides present in high level nuclear waste glass over its million year lifetime without any major degradation of the waste form or its properties. The glass waste form contains the vast majority of radiolytically created gases within the open structure of the glass.

5.1.2 Disadvantages of Glass Waste Forms

While the intent of this report was to emphasize the properties and limitations of the waste form, it is necessary to introduce some processing requirements in order to explain the limitations of glass. Numerous vitrification technologies are available which may reduce the problems with certain waste streams.^{8,9} The following are some of the limitations which are associated with glass final waste forms:

- Offgas system
- Leach resistance
- Limitations on organic materials in the feed
- Limitations on metals in the feed
- Solubility limits for certain elements
- Disposal of spent vitrification units
- Limited experience with LLMW form
- Waste stream compatibility
- Maintenance requirements.

Offgas System. Because vitrification is conducted at high temperatures [$\geq 1,000^{\circ}\text{C}$ ($1,832^{\circ}\text{F}$)] and gas producing materials may be included in the feed, an offgas system is usually required. In some cases, large amounts of liquid, including water, may slow the vitrification rate. Classes of offgas constituents which are commonly controlled during vitrification include the following:⁸

- Entrained feed material
- Toxic metals (volatile and semi-volatile)
- Organics
- Sulfates and sulfur oxides (SO_x)
- Nitrogen compounds (NO_x)
- Carbon monoxide (CO)
- Hydrogen, halides, and halogens
- Mercury, selenium, arsenic, cadmium, and lead.

These compounds are of concern for a variety of reasons and their emission may be limited or enhanced, depending on the type of vitrification technology employed.

Leach Resistance. Some of the key factors which effect the leach resistance are the glass composition, time the glass is in the solution, temperature, pH, redox potential of the leachate, ratio of surface area of sample to volume of solution (SA/V), radiation, and flow rates of the solution. Water attacks vitrified materials to some degree, although the attack is much less aggressive than that of alkali and acid attack. In a static environment, water attack quickly becomes alkali attack as the alkali present in the glass is extracted into the water and then takes part in the reaction. Attack by salt solutions is thought to correspond to the attack by water. Many chelating compounds attack glasses at a rate comparable to that of strong alkali. Citrate, gluconate, oxalate, tartrate, EDTA, and malate all attack glass in alkaline solution. Alkaline phosphate and acetate also attack glass readily. Hydrofluoric acid has the unique ability to dissolve silicate glasses, forming a solution of alkali fluorides and silicon fluorides.⁸ A recent qualitative observation¹⁰ indicated that certain borosilicate glasses may interact with humic acids.

Limitations on Organic Materials in the Feed. The presence of organic (carbon) materials creates reducing conditions in the glass which can change the valence state of the glass components. For example, this may lead to the reduction in the valence of multi-valent cations and in situations where the reduction is severe, can lead to the formation of metallic alloys or metallic sulfides precipitating in the glass. Certain toxic elements may also be reduced, which may make it more difficult to incorporate them in the glass structure. Changes in the pre-treatment, melting rate, or vitrification technology may be required.

Limitations on Metals in the Feed.^{11,12} The introduction of metals with the feed can create problems similar to those caused by excess organics. The metals may act as reducing agents for the glass and, depending on the vitrification process, may create various operating problems (e.g., shorting of electrodes, plugging of drains). Quantification of limits is dependent on choice of vitrification technology, waste stream composition, and specifications on the waste form.

Solubility Limits for Certain Elements. Certain chemical elements have limited solubility in specific glass structures. Typical examples are chromium, ruthenium, and noble metals. Again, quantification of the limits is dependent on the many factors and techniques involved in vitrification and the specifications of the waste form product.

Disposal of Spent Vitrification Units. The melter design and the melting conditions under which the melter becomes inoperative will determine whether melter disposal is a problem. Contaminated ceramic refractory may provide an additional waste material for disposal.

Limited Experience with LLMW Form. While there is extensive information on glass waste forms for high-level waste, there is limited information available at this time on the LLMW form. Research should be undertaken to determine whether the

information developed for the high-level waste form can be applied directly to the LLMW projects.

Waste Stream Compatibility. Because there has been little testing of LLMW with glass, there is limited understanding of how well glass will react with LLMW streams. The variability of the waste stream may require constant changing of additives to the glass. Thermal destruction of organics is recommended before a glass melter process.

Maintenance Requirements. It is possible that the wide variations found in the waste streams may necessitate frequent replacement of melter components. Cl is particularly harmful to melters.

5.2 HYDRAULIC CEMENT WASTE FORMS

Up until the early 1970s, cement was widely used in the commercial nuclear industry for solidifying simple radwaste streams, e.g., evaporator concentrates containing either sodium sulfate or boric acid solutions or slurries.¹³ Incomplete solidification or low waste loadings with boric acid wastes led to the use of simple additives like calcium chloride or the development of others like sodium silicate. The use of additives and modifiers increased the variety of wastes that cement could be applied to. Similarly, the Atomic Energy Commission (AEC) and its successor, U.S. Energy Research and Development Administration (ERDA), used cement to immobilize many of their small volume and miscellaneous fuel reprocessing waste streams, slurries, and sludges.¹⁴ These included nitrate solutions of various sorts, spent resins, metal sludges, off-gas scrub solutions and others. The large volume liquid wastes were typically placed in steel storage tanks for future processing.

In the last two decades, there has been an increase in waste streams being considered as candidates for immobilization using cement. However, the growing significance and importance of chemical, in addition to radionuclide, retention introduced by mixed wastes has increased the variety and complexity of waste matrices to be solidified, and waste product characteristics required. Several additives have been developed, and the use of slag material, fly ash, and lime modifiers to supplement portland cement has widened the range of waste types amenable to cement-based systems. The immobilizing agent in systems where the cement matrix is kept thin and transportable (pumpable) through piping systems is referred to as grout. Grout solidification systems have been installed and are presently in use at both the SRS and Hanford.^{15,16} These systems are used for immobilizing a low-level fraction of radioactive liquid tank wastes (mixed wastes). Non-grout cement systems are also being considered for treatment of various mixed waste streams.

5.2.1 Advantages of Hydraulic Cement Waste Forms

The advantages of using hydraulic cement based waste forms for immobilizing mixed waste include the following:

- Compressive strength
- Thermal cycling degradation
- Radiation stability
- Biological degradation
- Leach performance
- Immersion stability
- Free liquids
- Chemical durability
- RCRA compliance
- Compositional flexibility
- Processing and availability
- Ability to solidify chemical salts and salt solutions.

Compressive Strength. The NRC¹⁷ established a minimum strength of 0.34 MPa (50 psi) to conform with requirements of 10 CFR-61.56(b)(1) that a waste form will maintain its structure under disposal conditions. Computations made using soil densities and calculating the weight of the overburden established a value of 0.34 MPa (50 psi). This was changed to 0.41 MPa (60 psi) when the Hanford Site increased the depth of their disposal trench from 13.7 to 16.8 m (45 to 55 ft). However, cement-based concrete can exhibit 3.45 – 4.14 MPa (5,000 – 6,000 psi), so the NRC has recommended that cement-based waste forms exhibit a compression strength of 3.45 MPa (500 psi), which is considered a "maximum practical compressive strength," not just the "minimum acceptable compressive strength."¹⁷

Test summary results indicate that practically all compressive strengths for cement-based waste forms exceed 0.41 MPa (60 psi) and most also exceed 3.45 MPa (500 psi). Typical compressive strength results are in the 3.45 – 13.8 MPa (500 – 2,000 psi) range.

Thermal Cycling Degradation. Hydraulic cement requires water to setup. This water is typically bound chemically in the matrix to about 50%, and the balance is physically absorbed by the cement matrix. Once the cement waste forms are set and cured (28 days) the inherent water is well dispersed and fixed in the cement solid. Thermal cycling can remove and evaporate a small amount of the physically absorbed water, but the rest of the water in the matrix is typically stable and unaffected by freezing and thawing. This is illustrated by the shred/grout¹⁸ and resin-cement studies.

Radiation Stability. Gamma irradiation of cement waste products appears to have little or no degrading effects upon the waste form. The appearance remains the same, there is no evidence of any free liquid formation, and no measurable weight loss. Compression strength measurements tend to be lower than the initial strength value, but are still substantial.¹⁸

Biological Degradation. Bacteria and mold colonies typically exhibit little or no growth with cement-based waste forms. The wet culture material appears to help the cement cure and to exhibit higher compressive strengths.¹⁸

Leach Performance. Leachability is a key issue for waste form performance evaluations, so a number of studies have been done on leaching (see Section 4.2.1.2). Cement forms typically exceed the recommended leachability index of 6 for all radionuclides and most other chemicals of concern. Radiocesium, typically the poorest leach performer, achieves leach index values from 6 to 10.¹⁹ Cement modifiers and additives are often added to cement mixes to increase the waste form leach performance.²⁰

Immersion Stability. Most wastes solidified by cement have either soluble components or components that can swell in water. Immersion in water for 90 days provides adequate time for these water-interactive wastes to affect the waste form, either forming voids or causing contained species to expand against the cement structure. Either of these effects can cause the compressive strength to decrease. However, the cement waste forms can typically pass this test for reasonable waste loadings.¹⁸ Waste loading limits might be applied to ensure sufficient strength to pass the test.

Free Liquids. "Free liquid" formation for cement-waste forms can be avoided by the use of compositional phase diagrams or similar techniques. Compositional phase diagrams can be determined for identified waste streams that are very reproducible in determining the water to cement ratio that can't be exceeded.²¹ The diagrams typically show a compositional working range between the water to cement ratio required for basic mixing (the minimum water line established by the mixer operation) and the water to cement ratio defining the free liquid (maximum water) value. The use of well-mixed compositions within this composition range will produce a cement-waste product without free liquid. Substantial changes in waste compositions can alter the dimensions of the working range and require timely updates. Initial cement sets and the absence of "free liquid" is generally observed visually for cement waste forms other than grout. The waste solids are then sealed and stored for later disposal where the free liquid absence can again be checked by visual or non-destructive test (NDT) methods.

Chemical Durability. Hydraulic cement-based concretes are used in the construction business to build side walks, new homes, driveways, highways, bridges, skyscrapers, and, most notably, water storage dams. All of these structures are expected to last a number of years, particularly water storage dams, many of which were built in the 1930s and are now at least 60 years old. Hydraulic cement is compatible with nearly all earth related materials such as sand, clay, rocks, and most combinations of these materials. Various types of finely sized clays and soils dilute the cementing characteristics, but don't otherwise interfere with its setting properties. Chemical compounds in general act as a cement diluent. Only chemical compounds that react directly with the calcium or the trisilicate fractions of portland cement prevent it from setting properly. Other cements

act similarly. The cement immobilization of these interfering compounds or waste residues containing these compounds are quite limited as to their waste loading capacities. Compositional phase diagram determinations of these systems are useful in determining their use and maximum waste loadings.²¹

Cement is compatible with most sodium, potassium, and other alkali metal salts. Cement is moderately compatible with transition metal salts and less so with heavy metal ion salts. A high ratio of cement to salt is typically used for the immobilization of transition metal and heavy metal ion waste residues. Cement is also compatible with most waste solids, shredded or whole, and sets to form a concrete with the shredded solids acting as the aggregate. If the aggregate material is hard or strong, then the resulting product strength is largely a function of the surface area. The smaller the surface area to volume of the material being solidified per unit weight, the better the strength (gravel creates stronger concrete than sand).

RCRA Compliance. Section 4.2.2 shows that cemented soil, grouted salt waste (saltstone), and other cement-based waste forms can pass the TCLP test to meet EPA requirements.^{22,23} The TCLP test performance data on mixed wastes for cement waste forms are quite limited, but it appears that cement does immobilize and contain toxic metal compounds at least in trace quantities and sometimes in larger amounts. Slag cement appears to contain toxic metal compounds better than portland cement, and cement modifiers and additives can enhance test performance.

Compositional Flexibility. Compositional phase diagrams for various waste streams or residues are unique.²¹ Despite this uniqueness, each diagram generally indicates a substantial region of workable compositions. It is helpful, but not necessary, to have the diagram for selecting cement-waste compositions that can be used to prepare a disposable product. The application of a proper water-to-cement ratio is necessary and comparison of several different diagrams will generally show substantial overlap. This means that a selected water to cement ratio for immobilizing nitrate liquid waste might also be applicable to sulfate and phosphate wastes, and this is often the situation. Verification of these flexible regions is of course considered essential prior to actual waste application. Flexibility is generally best for those wastes of similar chemistry and physics.

Processing and Availability. A moderately-sized operation to prepare cement waste forms is generally easy to design and set-up. Off-gas treatment is not generally required, except for the typical slightly negative air balance system with HEPA filtration required of most radioactive operations. A continuous and/or batch mixer is required; waste holding, feed, and characterization tanks; drum or container handling equipment; and a waste storage area are generally necessary. The waste, after characterization and neutralization, if necessary, is fed into the mixer where it is mixed with the appropriate portion of cement and additional water if needed, and the resulting slurry placed into a shipping/disposal container. The cement sets-up into a solid within 24 hours (visual check). A variety of mixers can be used, including in-drum mixers, which eliminate or minimize clean-up. Large volume throughputs typically require a continuous mixer

which is operated around the clock; shutdown normally requires clean-up of the mixer with water and then solidification of that water at the start of the next campaign.

Cement, modifiers, and additives are readily available and easy to procure. Pozzolans such as fly ash and granulated furnace slag materials are not as readily available as cement, but are marketed worldwide. Mixing equipment is also readily available for many applications. However, specialty equipment, such as SRS's ashcrete mixer, is a special order.²⁴ The decades of industrial experience with cement systems is another advantage.

Ability to Solidify Chemical Salts and Salt Solutions. Cement-based materials can be used to solidify common salts such as chlorides, nitrates, sulfates, and phosphates.²¹ Compositional phase diagrams for the salts are unique. Hydraulic cement bonds with water that has the salt either dissolved or in suspension. The salt is then encapsulated by the cement. Solutions of course, are better encapsulated than slurries. In addition cements have some inherent basicity that decreases the solubility of most cations. This provides additional fixing characteristics that improve TCLP and leach performances for the less soluble compounds. The waste loading capacities of most salt residue wastes, however, are limited due to solubility considerations.

5.2.2 Disadvantages of Hydraulic Cement Waste Forms

The disadvantages of using hydraulic cement waste forms for immobilizing mixed waste include the following areas:

- Unsuitable waste streams
- Limited-use waste streams
- Porosity
- Chemical instability
- Sensitivity to chemical changes
- Leach resistance
- Decrease in physical strength
- Waste volume loadings
- Water immersion degradation
- Free liquid formation
- RCRA compliance on organic liquid wastes
- Heat of hydration.

Unsuitable Waste Streams. Waste streams that are difficult to solidify include boric acid and borates in general, tri-basic phosphate, volatile organics, and mercury metal. Use of Type III cement or set-accelerators works best for the immobilization of boric acid,²⁵ otherwise use of gypsum cement²⁶ or a non-cement-based solidifier is recommended. Boric acid, borates, and tri-basic phosphate interfere or react with the calcium trisilicate compound to prevent its setting and hardening. Acid phosphates on the contrary can be solidified and can be used as set accelerators.²⁷ Volatile organics and

mercury metal are not bonded by cement; therefore cement-based waste forms are not recommended for their immobilization. Ammonium salts react in the basic portland cement-water slurry to release ammonia gas, and they are not recommended. However, gypsum cements form a neutral matrix when mixed with water and can be used to solidify ammonium salts, and the salts are stable in a neutral pH medium. Aluminum metal reacts with hydraulic cement and generates gas and foaming during setting.

Limited-Use Waste Streams. There are waste streams for which waste loadings are limited. Below is a list of inorganic constituents present in waste streams that might inhibit cement hydration or degrade waste form integrity. Some have been discussed in the previous subsection.

- Arsenates
- Borates
- Chlorides
- Copper compounds (transition metal compound)
- Heavy metal salts
- Lead compounds
- Magnesium compounds
- Phosphates
- Spent resins
- Sodium compounds
- Sulfates and sulfides
- Tin compounds
- Zinc compounds.

Borates were discussed previously. Chlorides, when placed in contact with cement-based waste forms, generally exhibit a degrading action due to a significant change in phase diagram (chemical thermodynamics) making the exposed form unstable. Chlorides properly immobilized in a cement form become thermodynamically stable. Chlorides can be relatively soluble; waste loadings are limited because of this effect. Heavy metal ions, transition metal ions, lead cations, magnesium, and zinc compounds tend to displace or interfere with the calcium in the setting of cement. These materials tend to limit waste loadings. Optimum waste loadings are achieved by using as much cement as possible so as to minimize cation interference. Arsenates, phosphates, sulfates, and sulfides compete or interfere with the silicate anion of the calcium silicate cement compound. Again, optimum waste loadings can be achieved by keeping the cement ratio as high as possible.

Another type of waste residue that is limited in waste loading is spent organic and inorganic resins. It is limited to about 50 wt% or 75 vol% waste loading due to potential resin swelling and resin-water interactions.²¹

Porosity. Cement has an open cell structure that becomes porous as the cement sets and cures. Its porous nature can allow water to permeate its surface increasing the potential for radionuclide loss by leaching and ion exchange. The use of grout for mixed

waste disposal may be limited in its ability to meet environmental requirements which are still evolving with regard to nitrate, technetium, and toxic metal ions.²⁰ There are new commercial additives that promise to reduce cement porosity.²⁸ Compatible epoxies and polymer materials can sometimes be added to cement mixes to minimize permeability and porosity.

Chemical Instability. Portland cement cannot easily be used to solidify ammonium salts, which react with the basic cement slurry to form ammonium hydroxide, which volatilizes to ammonia gas. Use of gypsum cement is acceptable. Major constituents present in many radioactive, hazardous, and mixed waste streams can interfere with solidification chemistry and/or affect the waste form stability over time. Cement hydration mechanisms are upset by depletion in the solution of ion species which are essential for proper hydration, and by the release of undesirable ions. These exchanges affect the preparation of the encapsulated materials by acting on the rheology of the material (stiffening, false set, flocculation). The setting of the encapsulated material may be subsequently affected. The use of appropriate additives can usually minimize the latter effects.

Sensitivity to Chemical Changes. Cements can be sensitive to changes in waste chemistry and waste treatment. Substantial changes in waste composition, such as the addition of 10 wt% copper salt to a waste, or changes in mix proportions can alter the properties of the waste form. Selection of a different cementing agent may be appropriate with composition changes. The complexity of the reactions and mechanisms that occur during cement solidification are not always well understood, particularly if the waste composition is complex. Large volumes of waste generated at DOE facilities have been identified as "problem" wastes because they are either difficult to encapsulate or result in poor quality waste forms. Oils and non-volatile organic liquids have been listed in this category, but can be stabilized (solidified) by cement up to 35% by volume for non-toxic organics.²⁷ Both organic liquids and solids act as set-retarders for cement; addition of a set-accelerator or use of Type III cement may be required to overcome the set retarding effect.

Leach Resistance. EPA²⁹ reported test data that show an increase in leachability for arsenic sulfide waste when cement is used as a binder. Perry³⁰ indicates that for some cement waste forms, leachability can increase over time. Because the data on the tests are limited, no general conclusions can be reached.

Decrease in Physical Strength. Cement-waste blocks prepared from waste concentrates and sludges will generally exhibit less compressive strength than conventional concrete. The strength is particularly affected by the total salt content of the waste stream and of the cement block. Higher waste loadings generally reduce the strength of the final product. In addition, the cement may experience stresses not normally encountered in civil engineering, such as thermal excursions, gas generation, or radiation stresses. Concrete is generally a brittle material with high compressive strength

but low tensile strength. These characteristics make concrete waste forms prone to cracking unless the cement composition has been tailored for this purpose.³¹

Waste Volume Loadings. Waste streams immobilized by cement usually increase in volume. Waste loadings are poorest for solid wastes such as dry salts, ash, and other residues. Waste loadings are generally best for aqueous waste liquids since water is required as a part of the cementing process. Waste loading efficiencies are typically about 50 – 70%. Many other waste form options operate on the dry residue form and their apparent waste loadings look high when compared with cement.

Water Immersion Degradation. A problem associated with existing cement solidification processes for spent ion-exchange resins is that the cement waste products obtained sometimes swell and break apart when immersed in water for a long time. The heat evolved and the desiccant nature of cement causes the resins to dry out and contract after the cement has set. When immersed in water the resin beads swell due to absorption of water and the adsorption of soluble contents of the cement matrix. If the swelling force exceeds the containment (cement) force the product will break-up. Loss of waste form integrity has been reported in such cases.²¹ Limiting the resin loading to about 50 wt% (75 vol%) should provide sufficient cement bonding to hold the monolith together. Optionally, several resin pre-treatments have been proposed to minimize the resin swelling. These include intense resin drying, resin bead destruction, or other physical methods directed at the resin to prevent or minimize its swelling capability. Cement solidification of other materials that swell when exposed to water would need to be handled in a similar manner.

Free Liquid Formation. Veazey³² reported the appearance of free liquid within drums of nitric acid based evaporator bottoms solidified with Envirostone® cement. This phenomenon occurred 8 to 44 weeks after mixing. These drums were initially set hard and dry; the free liquid was subsequently discovered. Cement-waste-water systems form a phase system that can be determined and modeled.²¹ Use of phase diagram model and selection of a cement that will appropriately deactivate the waste should result in waste forms that repeatedly set-up properly with no free liquid formation. There are instrument systems that can be used to check filled and sealed waste drums for "Zero Free Liquid" verification.³³

RCRA Compliance on Organic Liquid Wastes. Incineration is the preferred (BDAT) EPA treatment for organic liquid wastes. Unfortunately, incinerators are limited in what they can accept and treat, depending upon the incinerator design. Certain mixed wastes with substantial amounts of organic liquids might not be processible by incineration and become a stabilization candidate. Gypsum and Portland cements can stabilize wastes with non-volatile organic liquids by physical encapsulation,^{26,27} but TCLP test performance for the resulting waste forms are not known or data on such forms is quite limited. The small amount of observations and data available indicate poor TCLP performance for non-polar organics. Cements typically do not bond to organic

compounds unless they are a polar compound or have a polar group attached. However, cement solidification does convert flammable or combustible organic liquids to flame resistant-type solids. More work in this area would be desirable.

Heat of Hydration. For very large pours (i.e. grout vaults) heat of hydration can present a problem, but for pours within a 55 gallon drum, this is not a problem.

5.3 SULFUR POLYMER CEMENT WASTE FORMS

5.3.1 Advantages of Sulfur Polymer Cement Waste Forms

Many of the advantages in using SPC as a final waste form are listed here and discussed in the following paragraphs:

- Immobilization of toxic metals
- Remediation capability
- Saving contaminated lead
- Compressive strength
- Resistance to thermal cycling
- Radiation stability
- Biological stability
- Leach resistance
- Immersion stability
- No free liquids
- No gas generation
- LDR compliance
- Compositional flexibility
- Operational advantages
- Chemical durability and subsidence resistance
- Minimum secondary waste stream
- Waste loading.

Immobilization of Toxic Metals. Table 4.2 lists the toxic metals and their compounds versus their individual boiling points. With SPC's top operational temperature being 149°C (300°F), only one compound on the list would volatilize in SPC. In contrast, a large percentage would volatilize in ceramics or glass. An advantage of SPC over high-temperature glass and ceramics is that SPC will stabilize several toxic metals and their compounds. High-temperature processes volatilize essentially all Hg, up to 90% of As and Se (and their compounds); up to 40% of the Pb and Cd compounds; and less than 10% of Ba, Cr, and Hg. Volatilized metals in the offgas must be contained, collected, and stabilized in a final waste form other than glass. SPC has successfully stabilized Pb, Cd, Cr, Hg, and As, and it has been concluded that SPC will accommodate other toxic metals at lower loadings.

Remediation Capability. Even though SPC and a given waste may fail the required tests, SPC can be remelted, reformulated, and resolidified to meet test requirements that were not met in a prior effort. Hydraulic cement systems cannot offer that capability, and high-temperature systems could do it but with a great deal more effort.

Compressive Strength. SPC has approximately twice the compressive strength of PCC in construction.³⁴ Construction-grade SPC can achieve compressive strengths as high as 89.6 MPa (13,000 psi).³⁵ Depending on the waste used, SPC can achieve compressive strengths in the range of 20 – 80 MPa (2900 – 11,603 psi).³⁶ SPC laden with MW^c has passed NRC's compression tests in every case, with an average of ≈ 27.6 MPa (≈ 4000 psi). As soon as SPC cools, it reaches the approximate strength that PCC reaches in 28 days and SPC continues to gain considerable strength for at least two years.³⁶

Resistance to Thermal Cycling. SPC laden with MW passed the NRC's thermal cycling test.³⁷ SPC has closed pores and therefore contains no water upon curing; even after immersion in water, it retains very little water to freeze.³⁶

Radiation Stability. [All of the tests mentioned here were irradiated to 20 MGy (10^8 rad).] When SPC that contained MW was tested, it passed the NRC's irradiation test.³⁸ In a proprietary commercial test, SPC laden with 80 wt% lead oxide passed the NRC test and actually gained compressive strength, exceeding test requirements by an order of magnitude.⁴² The Netherlands Energy Research Foundation conducted tests with SPC, PbI_2 , incinerator ash, and borate waste; they also noted that the test specimens gained strength during the test.³⁶ SPC and the inorganic waste contents are practically insensitive to radiation.³⁶

Biological Stability. SPC laden with MW passed NRC's biological stability test.³⁸ Because SPC is not damaged by biodegradation, it is replacing PCC in construction of sewer pipe in Austria,³⁹ and is being tested by the State of California for the same application.

Leach Resistance. SPC is highly resistant to leaching radionuclides and toxic materials and passed NRC's tests with high loadings of MW.^{38,40} SPC's low permeability assists in achieving a low leach rate. SPC has closed pores in the monolith; PCC forms about the same volume of pores, but they are connected and thus permit more water transport through the mass than does SPC.⁴⁵

Immersion Stability. SPC has passed all of its NRC immersion tests with MW. In order to pass with a 40 wt% loading of boric acid, 0.5 wt% of glass fibers were added.⁴⁴

^cThe MW tested included 43 wt% MW flyash (37 wt% zinc, 7.5 wt% lead, 5.5 wt% sodium, 2.8 wt% potassium, 0.8 wt% calcium, 0.7 wt% copper, 0.5 wt% iron, and 0.2 wt% cadmium), 40 wt% boric acid, 43 wt% bottom ash, and 40 wt% sodium sulfide.

No Free Liquids. SPC has no free liquids and no pore liquids upon solidification.^{35,41}

No Gas Generation. No gaseous radiolysis products have been detected, even during testing to 20 MGy (2E+09 rad).^{36,42} The formulation of gaseous radiolysis products was tested with SPC containing PbI₂, incinerator ash, and borate waste. The samples were irradiated to 20 MGy (2E+09 rad) in cylindrical aluminum cans sealed by welding. Extra effort was made to detect sulfur-containing gases like SO₂, H₂S, and volatile organic sulfur compounds. Gas chromatography was used to analyze the sample cans at the end of beta-gamma irradiation. No increase of pressure was noted and no gases, except those from the original contained air, could be detected. The same was true with alpha radiation. The samples gained compressive strength during the irradiation period.³⁶

LDR Compliance. Sulfur cement as a potential binder for encapsulation of mixed waste has been evaluated using actual mixed waste by BNL. Leach testing of mixed waste fly ash from INEL at waste loadings of up to 43 wt% in sulfur cement indicated that the TCLP leachate concentrations of toxic metals were well below EPA criteria. Maximum waste loading for this flyash in hydraulic cement was 16 wt%.⁴³

Compositional Flexibility. SPC is a thermoplastic. No activation agent is involved with solidification of SPC. When it cools, it solidifies. In contrast, PCC is recipe dependent; all of the chemistry for the involved components must be correct in order for solidification of PCC to occur.⁴⁴

Research and development by the U.S. Bureau of Mines and BNL resulted in a modified SPC that can now stabilize high loadings of waste types like dehydrated boric acid salts, incinerator hearth ash, MW fly ash, and dehydrated sodium sulfate salts, which have heretofore defied solidification and stabilization in PCC in any significant quantity.⁴⁴

Operational Advantages. SPC has an operational advantage over hydraulic cements. It can be held at temperature in the molten state for long periods of time with no known consequences. Hydraulic cements start degenerating within five minutes after the water is mixed in and must be poured with reasonable haste if a viable concrete is to be obtained. The mixer must be cleaned immediately after each pouring session or upon a shutdown, and the remaining waste, cement residue, and cleaning agents must be captured and treated in an independent effort. These problems were so troublesome that in-drum mixing systems have been adopted even though these all have problems too. Unnecessary water is never welcome in a nuclear facility, and water is not tolerated in SPC.

The primary operational dissimilarity between glass and SPC is the extreme difference in the temperature required to melt the two substances. SPC's working temperature range is 130 – 140°C (266 – 284°F); the working temperature of glass is some 1,000 – 2,000°C (1832 – 3632°F) higher. High-melt temperatures cause problems in design, fabrication, and operation of a feed, melt, pour, and offgas system where radioactive and hazardous contaminants must be contained. SPC has an advantage over

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glass because of its low melt temperature, low maintenance, and ease of operation. SPC is also easier to use than other thermoplastics, like polyethylene, because of SPC's low viscosity.^{34,44}

Chemical Durability and Subsidence Resistance. SPC is a durable, high-strength concrete that is resistant to abrasion and attack by sulfates and most acids and salts; conversely, PCC is destroyed by the same sulfates, acids, and salts.^{35,45,46} Creep in SPC is roughly half of that in PCC.^{37,46} Irradiation only strengthens SPC.^{36,42} In addition to elemental sulfur's natural stability, all of these factors suggest better durability and subsidence resistance.

Minimum Secondary Waste Stream. The secondary waste stream is limited to dust and gases that are collected by the offgas system. Being a low-temperature system, its emissions are quite small in comparison to vitrification and ceramic systems. Unlike hydraulic cements, there are no cement-and-waste residues to clean up and treat after completion of the pour.

Waste Loading. Comparative test results show that 6.0 times more sodium sulfate, 2.6 times more boric acid, 1.4 times more MW incinerator bottom ash, and 2.7 times more MW incinerator fly ash can be microencapsulated in SPC than in PCC and still pass the TCLP test.⁴⁴ The average was 3.2 times more waste in SPC than in PCC. BNL has successfully applied the SPC process for treatment of a range of LLW and MW, including sodium sulfate salts, boric acid salts, incinerator bottom, and flyash. Property evaluation studies were conducted to test waste form behavior under disposal conditions by applying test criteria established by the NRC and the EPA.⁴⁷

5.3.2 Disadvantages of SPC Waste Forms

While there are numerous advantages to SPC waste forms, there are also some disadvantages:

- Offgas system
- Disposal restrictions
- Waste limitations
- Flammability and explosivity
- Preheating disposal containers and waste.

Offgas System. An offgas system is required for SPC, although not nearly as large or complex as for a vitrification or ceramics system. Optimum pour temperature is between 130 and 140°C (266 and 284°F). Temperatures above 160°C (320°F) cause H₂S and SO₂ to be created; with normal safety precautions, reaching even 149°C (300°F) can and should be the limit as a safety margin. Offgas, or venting systems, are routine for all waste treatment systems.

Disposal Restrictions. SPC should not be used where continuous temperature in the disposal environment exceeds 100°C (212°F)--the Netherlands report suggests that temperatures of 110°C (230°F) not be exceeded.³⁶ Wastes stabilized in SPC should not be placed in disposal sites where strong alkali (over 10%) could be in contact with the waste.

Waste Limitations. SPC is not recommended for stabilization of waste exceeding a pH of 8 to 10. Wastes consisting of strong bases, strong oxidizing agents, aromatic or chlorinated hydrocarbons, or oxygenated solvents should be avoided.^{48,45} Although not tested, BNL recommends that SPC not be used to stabilize nitrate salts and other oxidizers without prior treatment because the mix could become reactive.⁴⁴ Organics are not favorably received; SPC does not adhere to organics.³⁶

Ignitability and Explosivity. Ignitability and explosivity must be considered when SPC is used; however, they are less of a concern than for elemental sulfur, and elemental sulfur is routinely handled safely in both the molten and solid state all over the world.

Preheating Disposal Containers and Waste. The disposal container and its inorganic waste contents have to be preheated both to prevent the molten SPC from freezing upon contact, and to drive off any liquids in the waste. Heating the waste and container allows the molten SPC to remain molten and seek out and fill the cracks and crevices.⁴⁹ Since the additional heating time for the SPC and waste mixture is known to cause favorable chemical alterations,³⁶ this heating action really is not a disadvantage.

5.4 CERAMIC WASTE FORMS

5.4.1 Advantages of Ceramic Waste Forms

There are many characteristics of ceramics which make them options for a final waste form:

- Compressive strength
- Resistance to thermal cycling
- Radiation stability
- Biological stability
- Leach resistance
- Immersion stability
- No free liquids
- Chemical durability
- Gas generation
- LDR compliance
- Compositional flexibility
- High waste loading
- Minimization of secondary waste streams

- Absence of large amounts of contaminated equipment
- Low-temperature processing of chemically-bonded ceramics.

Compressive Strength. Crystalline ceramics and glass ceramics generally have higher compressive strength than glasses, and chemically-bonded ceramics (unfired) generally have lower strength. However, the strength of all of these materials is adequate for this application.

Resistance To Thermal Cycling. Crystalline ceramics generally have higher resistance to thermal cycling than glasses. They also have higher thermal stability than glasses, which tend to devitrify when held at high temperatures [above 450° – 500°C (842 – 932 °F)]. Glass ceramics can have higher resistance if the thermal expansion coefficients of the crystalline phases are well matched to that of the glass matrix. Some of the phosphate-bonded ceramics, such as MgPO_4 , ceramics, are used as refractories.⁵⁰ It is probable that all of these materials could be made with sufficient resistance to thermal cycling for this application.

Radiation Stability. Crystalline ceramics are among the materials that have the highest radiation stability. Most are unaffected by ionizing radiation (beta and gamma). At very high concentrations of alpha decays (about 10^{18} per gram), some ceramics swell (dilate) more than glasses, and some become metamict^f, but these processes usually don't seriously affect retention of radionuclides. Both polyphase crystalline ceramics and glass ceramics can develop internal stresses at very high doses of displacement-type radiation because of differential swelling, but such doses are not likely to be present in LLMW. Both crystalline ceramics and glass ceramics are superior to hydraulic cements and organic binders in radiation resistance. Data are not available for chemically-bonded ceramics, but phosphate-bonded types are likely to have radiation resistance at least as high as hydraulic cements.

Biological Stability. Crystalline ceramics, glass ceramics, and chemically-bonded ceramics can be expected to have biological stability comparable to that of glasses.

Leach Resistance. Radionuclides are incorporated in crystalline ceramics, glasses, and glass ceramics on the atomic scale and are chemically bound in the waste form, rather than being only mechanically encapsulated. This produces higher leach resistance for these waste forms. Crystalline ceramics and glass ceramics generally have higher leach resistance than do glasses for radionuclides that are incorporated in crystalline phases. For those that remain in glassy phases, the leach resistance may be comparable to that of glass waste forms. Leach resistance of chemically-bonded ceramics will depend on the particular composition. Phosphate-bonded ceramics themselves are likely

f. Metamict - exhibiting lattice disruption due to radiation damage while the external morphology is retained.

to have good leach resistance because of the low solubility of phosphate minerals in water.

Immersion Stability. Crystalline ceramics and glass ceramics are essentially unaffected by immersion. Data are not available for chemically-bonded ceramics, but the immersion stability will probably be specific to the bonding system and the waste stream.

No Free Liquids. None of these three waste forms contain free liquids.

Chemical Durability. Crystalline ceramics can be in thermodynamic equilibrium with geochemical environments. A liquid phase that is in thermodynamic equilibrium with a solid phase contains a concentration of the solid equal to its solubility limit. Further dissolution of the solid can only occur if the liquid phase is replaced by new liquid that does not contain the species dissolved from the solid. In contrast, the interaction of a glass waste form is a much more complex process that involves the dissolution of glass components, the leaching of elements from the glass structure, and the formation of secondary phases that may be metastable and subject to further alteration with time. Predicting the long-term performance of the glass is dependent on understanding the kinetics of the various alteration processes and the fates of the various radionuclides after the glass has reacted to produce dissolved species or secondary phases. Glass ceramics are intermediate between crystalline ceramics and glasses in terms of thermodynamic stability. Chemically-bonded ceramics can be heated to convert the initial hydration bonds into stronger bonds (such as phosphate bonds). The chemical durability will depend on the waste stream composition.

Gas Generation. Crystalline ceramics and glass ceramics generate essentially no gas during storage. Gas generation from chemically bonded ceramics may occur, if the material is not heated to remove hydration bonds.

LDR Compliance. Crystalline ceramics, glass-ceramics, and chemically-bonded ceramics are not ignitable, corrosive, or reactive. They have not been tested by the TCLP. The chemically-bonded ceramics need to be tested for particular waste streams.

Compositional Flexibility. Any waste stream, from high-activity mixed-fission product and actinide wastes through hazardous wastes that contain little or no radioactivity, can be processed to produce a crystalline ceramic final waste form. The ability to design a ceramic waste form makes possible the choice of mineral phases that are particularly insoluble. With glasses, the choice is limited to glass-forming compositions. Ceramics can incorporate halides such as fluoride and chloride, which are common in some waste streams and have limited solubility in glass. Minerals such as MgF_2 and sodalite can be used for this purpose. Waste streams that contain large amounts of elements such as Mg, Al, Ca, Cr, Fe, and Ni and rather small amounts of Si and Na are particularly suited for ceramic waste forms. While glass waste forms can be made from these elements, they may require addition of large amounts of glass-forming

elements; this is inefficient and increases the volume of waste over that created using a ceramic waste form. Ceramic waste forms can incorporate reduced or noble metals as alloy inclusions. By contrast, these metals have been known to precipitate to the bottom of glass melters and interfere with joule heating. Low temperature ceramics appear to be very attractive for treatment of volatile metals.

High Waste Loading. Ceramics are capable of higher waste loading than glasses for waste streams that are low in glass formers, such as Si, and high in elements such as Mg, Al, Ca, Cr, Fe, and Ni. This means smaller quantities of additives are required to make the waste form, and lower volumes of waste result.

Minimization of Secondary Waste Streams. Glass melters tend to drive off volatile radionuclides and hazardous constituents which must be trapped and dealt with separately. In crystalline ceramic processing, they can be converted into non-volatile forms by low-temperature processing and can then be processed by hot pressing or by cold pressing and sintering, during which releases can be minimized. Chemically-bonded ceramics are processed at low temperatures, thus minimizing volatilization.

Absence of Large Amounts of Contaminated Equipment. Ceramic waste forms can be fabricated without generating significant amounts of contaminated equipment. In the case of glass, at the end of the melter's life, a rather large, radioactively contaminated object must be disposed of, while crystalline ceramics and chemically-bonded ceramics do not have this problem.

Low-Temperature Processing of Chemically-Bonded Ceramics. Chemically-bonded ceramic waste forms are processed at ambient and near ambient temperatures. Therefore, they do not have the problems associated with secondary waste streams and do not require offgas systems.

5.4.2 Disadvantages of Ceramic Waste Forms

The following items describe some of the disadvantages associated with ceramic waste forms:

- Compositional flexibility
- Particle size reduction
- Radioactive powders
- Offgas system.

Compositional Flexibility. The formulation of crystalline ceramic and glass ceramic waste forms is somewhat specific to the waste stream composition to be incorporated, as is that of glass and cement waste forms. This means that development and testing will be needed for each major waste stream to be incorporated. It also means that use of

crystalline ceramic and glass ceramic waste forms to incorporate small-volume waste streams of widely divergent compositions would not be a very efficient undertaking.

Waste streams containing large amounts of glass-forming elements, such as Si, P, and B, in comparison to the amounts of nonglass-formers, can probably be more efficiently converted to glasses or glass ceramics than to crystalline ceramics. Waste streams containing mercury as a contaminant could probably more effectively be incorporated in SPC than in ceramics, although formation of cinnabar may be a possibility, depending on the composition of the balance of the waste stream.

Particle Size Reduction. For crystalline ceramics, wastes must be of sufficiently small particle size to allow the desired chemical reactions to occur between the waste and the additives necessary to accomplish these chemical reactions. For some LLMW streams, this may not be problematic, but for others, this degree of size reduction is very difficult. Chemically-bonded ceramics can encapsulate waste with larger particle sizes.

Radioactive Powders. Processing of waste streams into a crystalline ceramic waste form generally involves handling of radioactive "powders." The median grain size and size range of the powder will depend on the process route chosen. Containment of fine powders is more difficult than for less finely divided material. Nevertheless, the French use a rotary calciner as part of their vitrification technology at La Hague, which produces powdered material, and they report no particular problems with this technology. In addition, INEL for many years used a fluid bed calciner, and LLNL built a pilot-scale model which gave a homogeneous product with a grain size of 2 mm (7.9E-02 in.) and essentially no fine particles. This material was used as feed in making SYNROC-D.

Offgas System. If volatile or semi-volatile organics or nitrates are present in the waste stream, considerable offgas will be produced in thermal processing, as is true for glass-forming processes. Both ceramic and glass waste form production will thus require an appropriate offgas treatment system. However, for chemically-bonded ceramics, there are no requirements for offgas treatment systems.

5.5 ORGANIC BINDER WASTE FORMS

Organic binders or polymer matrices are rapidly becoming candidate matrix materials for the immobilization, transportation, and storage of low-level waste. Thermoplastic materials and their associated technologies have been extensively studied and have been in use in various industries for over 50 years. Associated processes for solidification are relatively simple and readily adaptable. There are adequate data in the literature related to the short-term (90 days) characteristics of these polymers, obtained from tests conducted on laboratory scale specimens, as waste form materials. Thermoplastic and thermosetting polymers are similar in their chemical origin and basic organic structure, but their processing considerations and material properties are very different. Therefore, this section is comprised of various sub-sections highlighting specific advantages and

disadvantages associated with thermoplastic (bitumen and polyethylene) and thermoset (vinyl ester styrene, epoxy, and urea formaldehyde) polymers, along with the advantages and disadvantages common to both sets of organic binders.

5.5.1 Advantages of Thermoplastic Binder Waste Forms

The following are some of the advantages associated with thermoplastic binders:

- Solidification
- Compatibility/versatility
- Insensitive to waste chemistry changes
- Water resistant
- Low temperature processing
- Waste volume efficiency
- Leach resistance
- Water immersion testing.

Solidification. One of the principal advantages of thermoplastics is the fact that solidification is assured on cooling, whereas thermosets require a catalyst/promoter system to initiate the polymerization reaction and hydraulic cement systems require a hydration reaction for solidification.

Compatibility/Versatility. Thermoplastic polymers are highly versatile in terms of the waste streams and waste loadings that they can tolerate because thermoplastics are not susceptible to any chemical interactions with waste. Waste containment is achieved purely by physical microencapsulation in which waste particles are coated with the binder material. Polyethylene and bitumen are highly resistant to degradation by chemicals and have acceptable performance with the following waste streams: boric acid concentrate, alkali waste solution, and sludges.^{51,52} Polyethylene waste forms also perform better than portland cement or bitumens for nitrate salts, sulfate concentrates, and ion exchange resins.⁵¹ However, for bitumen, the pH level of the waste stream should be 7 or higher for optimum solidification.¹⁹ Polyethylene is also compatible with chemical environments such as various inorganic salts and dilute nitric and sulfuric acids.⁵²

Insensitive to Waste Chemistry Changes. Because there are no chemical reactions between binder and waste, characteristics of the thermoplastic-based waste forms are insensitive to waste stream chemistry changes. Unlike thermoplastic binders, solidification of cements requires direct reactions between cement and water and is sensitive to the physical and chemical characteristics of the waste streams. This constraint requires careful characterization of the wastes before solidification, pretreatment of the wastes if necessary, possible alterations to the additives, and additional testing to establish the performance of the cement-based final waste forms.

Water Resistant. Polyethylene is extremely resistant to attack by water.⁵⁶

Low Temperature Processing. Thermoplastic binders require relatively moderate [80° – 180°C (176 – 356°F)] temperatures that will not require elaborate offgas treatment. These process temperatures are low compared with those required for glass [>1,000°C (1,832°F)], which requires sophisticated offgas treatment.

Waste Volume Efficiency. Waste forms based on thermoplastic binders undergo a large volume reduction of aqueous wastes because of evaporation of contained water during solidification.⁵⁶ This results in high waste-volume efficiency for these binders compared with cement binders, which treat aqueous waste streams directly.

Leach Resistance. Bitumen has good nuclide retention properties for Cs and Sr^{57,58}; the leachability index for these nuclides ranges between 8.0 and 9.0. However, Co and ¹⁴C incorporated in bitumen have similar retention properties as Co and ¹⁴C in cements. Polyethylene has shown excellent leaching resistance for Na, ¹⁰⁶Ru, and ¹³⁷Cs.⁵⁹ Tests conducted at ORNL and BNL have shown that bitumen and polyethylene waste forms containing highly soluble salts such as sodium nitrate satisfy most of the RCRA and NRC leaching requirements.^{60,61,62,63} The EPA has indicated that asphalt binders (bitumen) decrease leachability more than ten-fold for As.⁶⁴

Water Immersion Testing. BNL data have shown that polyethylene waste forms containing 30 – 70 wt% nitrate salt loadings show no statistically significant change in unconfined compressive strength on completion of the 90-day water immersion testing.⁵²

5.5.2 Advantages of Thermosetting Binder Waste Forms

The advantages of thermosetting binders are summarized below:

- Compatibility/versatility
- Leach resistance
- Low temperature processing.

Compatibility/Versatility. Thermosetting polymers are not as versatile as thermoplastics because they require chemical reactions for polymerization; however, thermosets such as polyesters have good chemical tolerance towards the following waste streams: sodium sulfate and boric acid concentrates; ion exchange resins; alkaline waste solutions; sludges; decontamination wastes; and dry salts and ash.⁶⁵ Vinyl ester styrene is the only advanced polymeric binder that has been approved by the NRC for low-level waste solidification. Vinyl ester styrene has been used for encapsulation of nitrate wastes, soils, oily wastes, and Zircaloy claddings. Thermoset polymers, such as vinyl-ester styrene, epoxy, and water-extendable polyesters are also compatible with liquid waste streams without requiring pre-treatment or removal of moisture during processing.^{66,19}

Leach Resistance. Polyesters and epoxies have leachability indices for Cs similar to that of bitumen. However, polyesters are unable to retain ^{14}C . In particular, vinyl ester styrene has been found to have retention ability for nuclides such as Cs, Sr, and Co.⁶⁷ Vinyl ester styrene also has excellent leaching resistance for organic decontamination agents.⁶⁸ Leachability indices for EDTA have ranged from 9 to 11.

Low Temperature Processing. In general, thermosetting binders usually require room temperature processing similar to that of cements; thus they do not require elaborate offgas treatment. However, in processes such as UF, higher temperatures [$\approx 100^\circ\text{C}$ (212°F)] may be required.

5.5.3 Advantages Common to Thermoplastic and Thermosetting Binder Waste Forms

In addition to the specific advantages discussed above, thermoplastic and thermosetting binders have the following advantages in common:

- Waste loading capacity
- Resistance to thermal cycling
- Biological stability.

Waste Loading Capacity. Typically, organic binders have a waste loading capacity of 40 – 50 wt%, and loadings as high as 70 wt% have been achieved with polyethylene. In vinyl ester styrene, volumetric loadings can be as high as 2:1 for dry salts and ash waste/binder ratio.⁶⁵ This, in essence, compensates for the high cost of the polymer itself.

Resistance to Thermal Cycling. Resistance against repeated exposure to large temperature differences is desired for waste form materials. Based on ASTM test method B-553, bitumen, polyethylene, and vinyl ester styrene have been shown to maintain their strength.^{52,56,65} Both bitumen and polyethylene waste forms exposed to repeated thermal cycling according to the NRC test requirements have shown that there is no loss in strength or mechanical integrity of the waste form. Thermal cycling tests conducted on vinyl ester styrene waste forms show a slight drop in strength, but strengths are still high enough to satisfy NRC requirements.

Biological Stability. Biodegradation of organic binders is possible in some instances. For bitumen, research indicates the possibility of some bacterial growth but the extent of degradation is minimal. ASTM G-21 and G-22 tests conducted on polyethylene/sodium nitrate waste forms showed no fungal or bacterial growth.^{52,65} Similarly, for polyesters no change was observed after the waste forms were subjected to bacterial and fungal resistance tests.⁶⁵ However, for epoxies and UF, very little is known and further investigation is required.

5.5.4 Disadvantages of Thermoplastic Binder Waste Forms

The disadvantages of thermoplastic binders are as follows:

- Physical stability
- Pretreatment
- Incompatible waste streams
- Flammability
- Leach resistance.

Physical Stability. Polyethylene is susceptible to environmental stress cracking when exposed to ultraviolet (solar) radiation and oxygen.⁵² This phenomenon should not significantly impact polyethylene waste forms since they will be shipped and stored in containers, and will not be exposed to sunlight during permanent disposal. Further, the effects of environmental stress cracking are limited to several millimeters of the surface of the material and would not affect a large mass such as a polyethylene waste form.

Polyethylene is extremely resistant to attack by water and has passed water immersion tests, but may develop stress cracks in the presence of such polar liquids as metallic soaps, organic esters, liquid hydrocarbons, and silicone fluids.⁵⁶ Bitumen has a problem of swelling and cracking because water can diffuse into the waste forms loaded with dehydrated salts or ion-exchange resins.

Pretreatment. Thermoplastics are compatible with a wide range of waste types, as discussed above; however, they cannot process aqueous wastes without pretreatment or removal of moisture during processing.

Incompatible Waste Streams. Polyethylenes deteriorate in the presence of free halogens with dehydrated salt or ion exchange resins, and organic liquids (ketones).⁶⁹ Polyethylene is incompatible with waste streams containing compounds such as benzene, gasoline, lubricating oils, alcohols, and xylene.⁵² Bitumen has problems with organic liquids. Oils tend to emulsify bitumen and should be limited to less than 1% of the feed stream. Dehydrated salts such as sodium nitrate, sodium sulfate, and magnesium chloride can also be incompatible with bitumen.^{19,61} EPA data show arsenic sulfide waste increased in leachability when polyethylene binders were used.⁶⁴

Flammability. Bitumen is susceptible to fire during processing, transportation, storage, and disposal.

Leach Resistance. Arsenic sulfide waste shows an increase in leachability when polyethylene is used.⁶⁴ Swindlehurst⁶¹ reported that bitumen, when used in a sodium nitrate-based waste, failed the ANS 16.1 leaching test for chlorine.

5.5.5 Disadvantages of Thermosetting Binder Waste Forms

The disadvantages of thermosetting binders as a final waste form option are summarized below:

- Waste stream properties must be monitored
- Incompatible waste streams
- Limited shelf-life
- Free liquids.

Waste Stream Properties Must Be Monitored. Because thermosets involve other components, such as catalysts or promoters, to polymerize and solidify the binder material, there is always the potential for chemical interaction between the binding agent and chemicals in the waste stream. This interaction can retard or prevent solidification. Therefore it becomes critical to monitor waste stream properties and to make necessary changes for optimal solidification.

Incompatible Waste Streams. Thermosetting polymers such as vinyl ester styrene have been found not to perform with wastes containing more than 1 wt% C, Zn, Cu, and metal salts.⁷⁰ UF has similar compatibility with waste streams as polyesters, except that it also has limited loading capacity for sodium sulfate wastes.

Limited Shelf Life. Thermosetting binders, such as vinyl ester styrene, have a limited shelf life because of premature polymerization at ambient and elevated temperatures. Therefore, refrigeration, aeration, and filtration of binder materials may be required to prolong their useful life.

Free Liquids. Free-standing water is usually not present in thermosetting-binder-based waste forms, but may occur if the emulsion is not performed at the proper shear rate or if the waste-to-binder ratio exceeds maximum limits. In some polymers, such as UF, free water occurs because of the condensation reaction during polymerization. Free-standing water is acidic in UF and can corrode the storage container. This is the major reason why UF is not commonly used as a solidifying agent.

5.5.6 Disadvantages Common to Thermoplastic and Thermosetting Binder Waste Forms

Thermoplastic and thermosetting binders have the following disadvantages in common:

- Compressive strength
- Radiation stability
- Thermal stability.

Compressive Strength. Compressive strengths of the waste forms are dependent on the type of waste incorporated and the waste loading. Typically, organic binders have lower strengths than cements and glasses, and thermosetting polymers generally have a higher compressive strength than thermoplastic polymers. The strength of organic binder waste forms is well above the criterion established by the NRC for commercial wastes. Compressive strengths as high as 27.6 MPa (4,000 psi) have been achieved in polyethylene loaded with 50 wt% ion-exchange resin waste.⁷¹ Bitumen has a relatively low compressive strength and a tendency to creep and deform under pressure at ambient temperatures. Vinyl ester styrene waste forms exhibit some of the highest strengths 13.9 – 55.2 MPa (2,000 – 8,000 psi) among the polymeric materials for a variety of waste types and loadings.⁶⁵ In contrast, in glasses and cements, strengths as high as 55.2 MPa (80,000 psi) and 68.9 MPa (10,000 psi), respectively, are observed.⁵⁶

Radiation Stability. Susceptibility to radiation damage is a function of the type of polymer. Radiation stability of organic binders ranks below that of cements and glasses. Gamma-irradiation with high doses [10^6 Gy ($\approx 10^8$ rad)] can cause moderate to severe damage and the release of radiolytic gases in organic binders. Damage depends on the amount and type of waste solidified, dose rate, and presence or absence of oxygen. External irradiation causes waste forms to become brittle, swell, release radiolytic gases, and degrade in strength and leaching resistance.^{56,65} However, in certain polymers such as polyethylene, high doses of gamma radiation [10^6 Gy (10^8 rad)] leads to formation of additional bonds through crosslinking. The net result is increased strength, lower permeability and leachability, and better resistance to chemicals.⁶⁶ In general, thermosets have better radiation stability than thermoplastics because of their crosslinked structure.

Thermal Stability. Exposure to heat is deleterious to most organic binders and can lead to slumping of the waste form at moderately high temperatures. Moreover, addition of oxidizing wastes in bitumen results in a lowered flash point of the binders. Organic binders are more flammable than cements and glasses. However, at storage and transportation temperatures and in the absence of open flame, they are not a fire hazard. Polyethylene has been rated as slightly flammable by the National Fire Protection Agency and is self-extinguishing below the flash temperature.⁵² Vinyl ester styrene waste forms also do not support combustion and char when exposed to burning fuel oil. But, their process is extremely flammable and requires fire protection. Epoxies, on the other hand, are nonflammable and have self-extinguishing properties.⁶⁵

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6. DEFICIENCIES AND GAPS IN DATA

The consensus of the FWF TASR Working Group is that there are applicable tests for measuring many important waste characteristics. However, the tests are best suited to a comparison of different waste forms. A substantial research program will be needed to validate the test methods. The results of each method must be compared to measurements made on field-disposed waste forms. Research will also be needed on methods for assessment of waste form performance (risk reduction). These two programs need to be coordinated to ensure that characteristic tests provide the data necessary to conduct the performance assessment. Validation of both characteristic tests and performance assessments should include measurement of the changes that take place as the waste form undergoes weathering over decades, to establish the long-term durability of the waste forms. This research will lead to the development of test methods that address chemical stability, solubility, and compositional flexibility and to provide data for generic PAs (arid/non-arid).

To determine which candidate waste forms would be most appropriate for a given waste stream, certain aspects of the waste stream's chemical composition must be known. Currently, there is little detailed information about DOE's LLMW waste stream composition; therefore, only guesses can be made about how to best match waste forms to waste streams. Thus, waste form development cannot be efficiently focussed on the needs.

In general, the following are gaps and deficiencies which are common to all of the waste forms discussed in this TASR:

- Lack of a systems approach in analyzing and evaluating the FWF requirements based on the waste streams to be processed
- Lack of a uniform set of tests and performance criteria to compare and evaluate competing FWFs
- Lack of a list of specific simulated wastes that represent the MWTP site-specific waste streams to enable more direct comparisons of FWF options
- Lack of real-time field monitoring correlations with the models used in PA analysis
- Lack of guidelines for screening FWF applicability to particular waste streams.

6.1 GLASS WASTE FORMS

While glass has been identified as the waste form which can stabilize a large portion of the MWTP waste streams, there are still areas in which there is information yet to be obtained. These are identified as the following gaps and deficiencies:

- Evaluation of LLMW glass waste forms
- Vitrification technologies
- Induction heating
- Melting technologies.

Evaluation of LLMW Glass Waste Forms. The vast majority of literature on glass waste forms is devoted to the high-level radioactive borosilicate glass. While a great deal of this information can be indirectly applied to LLMW glass waste forms, additional experimental evaluations are needed. There was a modest amount of information available describing the vitrification of glasses containing varying levels of toxic elements in the presence of metals, organics, chlorides, or sulfides.

Vitrification Technologies. Additional information on alternate vitrification technology should be obtained. The operation and limits for electric joule heated, in situ, and gas-fired melters is reasonably well documented.

Induction Heating. The use of induction heating for mixed low-level waste has not been studied. Induction heating of high-level waste is represented by the French AVM process. Because induction heating is also used in commercial specialty glass and specialty metals manufacturing, it is potentially applicable to hazardous and radioactive wastes, particularly those containing metallics and organic materials.

Melting Technologies. Electric arc heating was first developed for the metals industry and later adapted to the melting of high temperature refractories. Microwave vitrification is still in an early stage of development. While some initial work is being planned, there is little information on the problems and advantages of these melting technologies. These types of melters have the potential of melting inorganic materials in the presence of metals and reducing materials.¹

6.2 HYDRAULIC CEMENT WASTE FORMS

Present applications need new and better data on problem waste streams, as well as good application examples. Problem waste stream deficiencies and gaps are summarized in Table 6.1.

The gaps and deficiencies for hydraulic cement waste forms include the following:

- Understanding the basic solidification mechanism
- Limited data on NRC test performances with mixed waste streams
- Limited data on EPA (TCLP) test performances with mixed waste
- Problem waste streams
- Long term durability of cement waste forms
- Cement binder reactions with waste species.

Basic Solidification Mechanisms. Hydraulic cement waste form difficulties are typically traced to specific problems of individual waste streams. The performance of particular binder formulation and engineered applications have been highlighted. There appears to be a lack of test data from basic research and development programs to the chemistry of cement immobilization mechanisms. Such analyses will aid in declaring

Table 6.1. Problem waste stream deficiencies and gaps for hydraulic cement

Arsenates	- Waste loading limits - TCLP performance
Borates	- Not recommended for Portland cement without additives - Waste loading limits with additives
Chlorides	- Waste loading limits - Leachability - TCLP performance
Copper Compounds	- Additives to be used - Waste loading limits
Heavy Metal Salts	- Waste loading limits - TCLP performance
Lead Compounds	- Waste loading limits - TCLP performance
Magnesium Compounds	- Additives - Waste loading limits
Organics	- Polarity effects - Waste loading limits per type of organic - TCLP performance - Leachability - Strength
Phosphates	- Waste loading limits - Optimum waste pH
Spent Resins	- Pretreatment - Waste loading limits per specification
Sulfates and Sulfides	- Leachability - Waste loading limits - TCLP performance
Tin Compounds	- Waste loading limits
Zinc Compounds	- Waste loading limits

with fair certainty the final chemical nature of the ions and molecules being stabilized. The confidence gained by a definitive understanding of the atomic and molecular locations of hazardous constituents in final waste forms will assist in the ability to predict correctly the long-term effects of burial disposal.

The safe treatment/disposal of DOE defense waste is a unique problem because of the range and complexity of waste constituents. Current laboratory analyses of wastes stored at Hanford and other sites are generally available but most of these solutions and sludges are slated to go through pretreatment steps for safety and other reasons. Pretreatment methods are still being developed and a better understanding of their resulting waste stream composition is needed before final cement solidification techniques can best be applied. These questions can be answered by knowledge of the bonding mechanisms listed above (chemical, physical, hydrate, etc.) for those waste residues passed along by pretreatment processing.

NRC Testing of Mixed Wastes. Mixed wastes are a relatively recent issue (1980 RCRA legislation). Considerable NRC-type testing has been carried out on low level radioactive waste, but data at present is still quite limited on mixed wastes. It would be very useful for planning purposes to have available extensive NRC waste form performance testing on major mixed waste streams. This is not happening at present to any significant degree nationwide.

EPA Testing of Mixed Wastes. Performance of mixed waste disposal forms for EP toxicity and TCLP tests are limited. Hanford and SRS have tested some on their wastes going to grout or saltstone.^{2,3}

Problem Waste Streams. There are a number of waste streams indicated in the literature or the NRC position paper⁴ that are termed "problem waste streams" for cement waste forms. These problem waste streams include arsenates, borates, chlorides, copper compounds, heavy metal salts, lead compounds, magnesium compounds, organics, phosphates, spent resins, sulfates and sulfides, tin compounds, and zinc compounds. This might mean problematic interferences, hydration interaction, poor selection of water-to-cement ratios, etc. It does not necessarily mean that cement cannot be used with these waste forms, but that one should use caution to make sure the cement is going to set properly and provide the characteristics desired or required, or that waste loadings might have to be limited to some set value. Fischer used a portland cement mortar to successfully immobilize chloride salts.⁵ Others have immobilized sulfates, phosphates, transition metal salts, etc. Waste form performance data, good or bad, are needed with streams that are on the problem list to better evaluate the use or non-use of cement.

Long-Term Durability of Cement Waste Forms. Most people are acquainted with use of cement in the present world and has a feel for its short term durability. However, the long term durability of cement is in question. Some ancient cements or concrete have exhibited good chemical durability, but they are not compositionally equivalent to present day commercial cements such as portland cement. This might be an area of

concern if cement is used for disposal of waste containing substantial loadings of long half-life radionuclides not protected by a geologic barrier.

Cement Binder Reactions with Waste Species. The effects of the waste species on cement binder reactions need assessment. McDaniel⁶ has repeatedly stressed the need to understand the chemistry and microstructure of cement-based waste forms for the following:

- Predicting leachant performance
- Developing better leach tests
- Learning more about waste form durability
- Designing better performing waste forms.

More fundamental knowledge will help explain waste form performance, assist in extrapolation from one application to another, and predict cement waste form performance in the future.

6.3 SULFUR POLYMER CEMENT WASTE FORMS

SPC has successfully passed the NRC and EPA laboratory tests with some difficult wastes at high loadings, thereby making it a strong candidate for hazardous, mixed, low-level, low-level greater than class-C, transuranic, and some high-level wastes. In spite of the successes, the testing and development of SPC as a final waste form is in its infancy. Deficiencies and gaps are listed here and discussed in the following paragraphs:

- Stability
- Effects of prolonged heating and remelting
- Offgas residuals
- Waste loading
- Problem waste streams
- SPC formulation

Stability. Elemental sulfur is a very inert element, and tests suggest that SPC is also durable in environments that would destroy PCC.⁷ Microscopic examination and materials analyses are needed to help answer the longevity question.

Effects of Prolonged Heating and Remelting. SPC can be maintained in the recommended pouring temperature range in a mixer for long periods of time and still remain plastic and workable. From an operational viewpoint that is very important; however, there is no information available on the effect of prolonged heat on SPC and specific waste contents.

It has been postulated that SPC-and-waste packages that failed their tests can be remelted, and more SPC and additives can be added. When repoured they are expected to pass the required tests. Tests to verify this concept have not yet been conducted.

Offgas Residuals. With all the technical reports examined on waste stabilization, none were directed toward the offgas contents, other than to say that H_2S , SO_2 , and volatile organic sulfur compounds are created at temperatures exceeding $160^\circ C$ ($320^\circ F$).⁸ Efforts are necessary to determine what compounds are trapped in the offgas system, and to determine methods to extract and treat such compounds to a FWF.

Waste Loading. Lead, mercury, arsenic, and cadmium have been combined with SPC in what were believed to be fairly high loadings.⁹ The loading capabilities for those toxic metals and other toxic metals in SPC that will pass the TCLP test are unknown.

Irradiation tests of 80 wt% lead oxide combined in SPC were recently completed at Oregon State University. The samples gained approximately 6.9 MPa (1,000 psi) in compressive strength while being subjected to 10^6 Gy (10^8 rad) and there were no gas emissions.¹⁰ However, no TCLP tests were conducted on the samples. It is yet to be determined how much lead can be added to SPC and still allow the samples to pass the TCLP test.

Problem Waste Streams. BNL does not recommend combining nitrate salts with SPC because the two compounds, when combined, could cause a reactive mixture.⁷ There have been no known R&D efforts in this area, and considering the problems at RFP, this is an important subject needing research.

There are many waste combinations that have not been tested with SPC. A variety of waste combinations need to be studied to determine the effectiveness of SPC as a final waste form.

SPC Formulation. None of the successes cited in this document were achieved by changing the ratios of dicyclopentadiene and oligomers of cyclopentadiene in SPC. The SPC formulation was optimized for the construction industry rather than for the waste stabilization industry. SPC was originally tested with dicyclopentadiene and oligomers of cyclopentadiene in equal quantities from 5 wt% to 22 wt% (brittle at the lower end and rubbery at the upper end). SPC displayed its best commercial concrete characteristics when 2-1/2 wt% of each of the two additives were used. The range between 5 and 22 wt% leaves much room for experimentation, since the NRC requires only 3.4 MPa (500 psi) compressive strength. The Canadian formulation for Sulfurcrete offers another potential not yet explored.

The addition of 0.5 wt% glass fibers to a mix of SPC and boric acid allowed a 40 wt% loading of boric acid to pass the immersion test. It has not yet been determined whether or not that same tactic may improve the immersion test results with other wastes.

6.4 CRYSTALLINE CERAMIC, GLASS CERAMIC, AND CHEMICALLY-BONDED CERAMIC WASTE FORMS

The following items have been identified as gaps and deficiencies on our information related to ceramics;

- Formulations
- Properties of ceramic waste forms
- Waste stream pretreatment
- Waste loading
- Accommodation of waste stream variation
- Bonding chemistry for chemically-bonded ceramics.

Formulations. As noted earlier, the formulation of crystalline ceramic and glass-ceramic waste forms is somewhat specific to the waste stream to be incorporated. Since they have not been applied to mixed waste streams in the past, it is not known what the detailed formulations should be to best incorporate particular mixed waste streams.

Properties of Ceramic Waste Forms. Although the properties of ceramic waste forms for mixed waste show promise of being very good based on previous work on high level waste, these properties need to be experimentally measured for the mixed waste streams of interest.

Waste Stream Pretreatment. An important question is the degree of pretreatment that waste streams need to produce an acceptable ceramic waste form. In particular, the amount of particle size reduction required and any redox adjustment needed must be determined.

Waste Loading. For a particular waste stream, the maximum allowable waste loading is another unknown parameter, as is the tolerance of the waste form for the type of radiation effects that will be produced by the radionuclides incorporated.

Accommodation of Waste Stream Variation. Another area in which more needs to be known is the ability of a ceramic waste form to accommodate compositional variations in the waste stream for which it is designed.

Bonding Chemistry for Chemically-Bonded Ceramics. Bonding chemistry and immobilization processes in the various chemically-bonded ceramics need to be established.

6.5 ORGANIC BINDERS

No single binder material can be used universally for the wide variety of DOE LLMW streams that must be encapsulated. Choice of binder material depends both on its compatibility with the waste stream and appropriate performance of the final waste form. Even though organic binders are considered to be well-developed and are used in various applications, further research and development is needed in the following areas.

- Identification of compatible and problem waste streams
- Maximization of radionuclide retention

- Compressive strength development
- Characterization of catalyst/waste stream interactions for thermosetting binders
- Chemical durability
- Flammability.

Identification of Compatible and Problem Waste Streams. Identification and documentation of waste streams that work or cause problems with a specific binder system is currently not available. It is important to determine and establish which hazardous elements/compounds need to be avoided for a particular binder system. In particular, effects of various hazardous metals, such as As, Cd, Cr, or Hg, on the binder performance need to be resolved. For example, leachability of As can be substantially reduced from hazardous wastes encapsulated with asphalt. However, compatibility and leachability of As in other organic binders and their corresponding waste form characteristics is not known.

Maximization of Radionuclide Retention. While radionuclide retention for most organic binders is far better than conventional waste form materials, improvements in leachability of both hazardous and radionuclide constituents may well be possible. For example, researchers at BNL have shown that addition of sulfide compounds reduces the leachability of hazardous metals from sulfur cements. Using a similar approach, additives to bitumen and polyethylene binders may lead to the formation of insoluble species that incorporate toxic metals, thereby improving the radionuclide retention properties of the binder.

Compressive Strength Development. Bitumen tends to deform under application of loads due to its low strength. In addition, long-term exposure to water can lead to swelling and cracking of bitumen-based waste forms. This limits its range of applications as a waste form material. Improvements in mechanical properties of bitumen, as well as for other organic binders, have to be made by selection of proper additives.

Characterization of Catalyst/Waste Stream Interactions for Thermosetting Binders. Compatibility of the binder and waste stream is crucial for thermosetting polymers. Thermosets run a risk of not setting because waste stream chemicals may inhibit polymerization. Incomplete polymerization affects several performance properties of the final waste form. Currently, characterization of waste streams is necessary to avoid these problems. In addition, pre-treatment technologies may be needed to enhance the encapsulation process. A database of specific interactions between waste stream components and various thermosetting polymers is needed.

Chemical Durability. For bitumen-based waste forms with loadings of nitrate salts, spent ion-exchange resins, and evaporator concentrates, there is a need for additional information regarding chemical and compositional durability and solubility. Similar gaps are present in the literature, as summarized in the data sheets, for other organic waste

forms. These issues must be addressed before a particular solidification medium can be commercialized for a specific waste stream.

Ignitability. Ignitability can be a concern for some polymers in both their pure and final waste forms. Further investigations are required to improve and establish flammability characteristics of the organic binders encapsulating various waste streams to widen their range of applications.

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7. CONCLUSIONS

Based on the information reviewed for this TASR, it is apparent that several potentially viable options exist for producing a FWF from DOE LLMW. The MWIP is considering the enhanced (glass) waste form as a preferred alternative to cement as a FWF. Because glass waste forms resulting from vitrification processes are not universally effective on all of DOE's LLMW streams (e.g., volatile metal components, chloride salts), other FWF options need to be developed and available for contingency use. These candidate technologies have not yet received extensive or comprehensive evaluations for the wide variety of wastes, nor have comprehensive evaluations been made for specific waste streams.

Desirable properties and characteristics of acceptable FWFs for LLMW can be defined in general terms; however, site specific PAs will provide the quantitative measures of FWF performance. Preparation of generic PAs for arid and non-arid sites will aid in identifying data requirements for FWF performance evaluation and will provide quantitative selection criteria. Models for long-term durability and leach resistance will require validation before FWF performance can be included in PA evaluations.

Uniform tests for FWF evaluations and/or selection have yet to be agreed upon. Many tests and evaluations of FWF options have been conducted to determine FWF properties. These tests and evaluations were conducted using a variety of test procedures to establish indices for FWF performance; therefore, it is difficult, if not impossible, to make meaningful comparisons between different FWFs, or even between tests conducted on a single FWF, based on previous data.

Evaluations between different FWFs are also difficult because various waste streams have been used in the FWF studies. For example, glass and ceramics have primarily been evaluated using simulated high-level waste streams, while PCC, SPC, and organic binders have been tested and evaluated for a variety of very specific waste compositions that are not necessarily representative of the DOE's LLMW streams. No FWF discussed in this TASR has been tested or evaluated for the wide variety of DOE's LLMW streams.

The overall effectiveness of a particular FWF can only be made by evaluating the FWF for specific waste streams. Only by using a system-analysis approach to determine the interdependence of waste streams and waste processing may the effectiveness of a FWF be established. Since a rigorous systems-analysis is beyond the scope of this TASR, a generic systems-analysis was used to define the FWF evaluation criteria. Figure 7.1 illustrates this generic system; the unit operations within the dashed box indicate those operations that are dependent on the FWF option. Unit operations outside the dashed box will remain essentially the same, regardless of the FWF option chosen. The operations which are dependent on the FWF options have been included in the evaluation criteria shown in Table 7.1. This evaluation was made by members of the FWF TASR Working Group. The results of the evaluation of each FWF, by waste stream, are also given in Table 7.1. Descriptions of each waste stream may be found in Appendix A. The following conclusions were drawn from this analysis:

Fig. 7.1 Generic final waste form system

Code Number	Mixed Waste Category	Glass		Hydraulic Cement	Sulfur Polymer Cement	Ceramics		Organic Binders			% of Total WS	
		Melter	Plasma Arc Furnace			Crystalline	Chemically Bonded	Polyethylene	Thermoplastic Bitumen	Polyesters		Epoxy Thermosetting
W100	Aqueous Liquids	PN24/6	K	P	PN2	PN2	K	PN2	PN2	P	K	3.04%
W110	Corrosive - Acids	PN2/6	PN2	PN4	PN2	PN2	K	PN2	PN2	K	N1	25.43%
W120	Corrosive - Bases	PN2/6	PN2	P	N1	PN2	K	PN2	PN2	K	N1	0.19%
W130	Corrosive - Cyanide	PN2	PN2	K	N1	N5	N3	PN2	PN2	N1	N5	0.00%
W150	TC-Metals	PN2/6	PN2	PN4	PN2	PN2	K	PN2	PN2	K	N3	4.06%
W160	TC-Organics	PN2/6	PN2	K	K	PN2	K	K	PN2	K	N3	0.51%
W180	Hg Containing Solutions	N4	N4	PN4	K	N5	K	N5	N4	K	N3	0.07%
Subtotal												33.32%
W200	Organic Liquids											
W210	Non-Halogenated Organic	PN1	P	PN1	PN1	PN1	K	PN1	PN1	P	K	1.72%
W220	Halogenated Organic	PN13	PN5	PN13	PN13	PN13	N2	PN13	PN13	K	K	1.31%
W230	Scintillation Cocktails	PN1	K	PN1	PN1	PN1	K	PN1	PN1	K	K	0.28%
W280	Hg Containing Organic	N4	N4	N14	K	N5	N2	N4	N4	K	N3	0.01%
Subtotal												3.31%
W300	Inorganic Solids											
W310	Wet Inorganic Solids											
W311	Sludges, Filter Cakes, & Residues	P	K	D	D	P	K	P	P	P	K	12.71%
W312	Absorbed Liquids	P	K	PN1	PN1	N5	N2	PN1	PN1	K	K	0.22%
W314	Salt Cakes	N4	K	N1	N1	PN45	K	D	D	K	N12	0.09%
W320	Dry Inorganic Solids	PN4	K	N1	N1	PN45	P	P	P	K	K	0.96%
W321	Processing Salts	K	K	N1	N1	PN45	K	D	D	K	K	0.12%
W322	Cemented Sludges	P	P	PN1/4	PN2	P	K	PN2	PN2	P	P	7.99%
W323	Ash, Dusts, and Particulates	P	P	D	D	P	K	K	K	P	P	0.94%
W324	Soils	D	D	D	P	P	K	K	K	P	K	0.51%
W325	Glass	D	D	PN1	K	N1	N2	K	K	K	K	0.43%
W326	Ceramic Crucibles, Bricks, Media	P	K	N1	K	P	K	K	K	K	K	0.60%
Subtotal												24.59%
W400	Metal Wastes	N2	P	N2	N2	N2	N12	N2	N2	N2	N2	7.04%
W420	Non-Ferrous Metals	N2	P	N2	N2	N2	N12	N2	N2	N2	N2	0.01%
W430	Mercury	N4	N4	N3	K	N4	K	N2	N4	K	N3	0.01%
W440	Lead Shapes	N2	N4	N3	N2	N2	N12	N2	N2	N2	N23	1.23%
W450	Activated Lead	N2	N4	N3	N2	N2	N12	N2	N2	N2	N23	0.00%
Subtotal												8.31%
W500	Organic Solids											
W510	Wet Organic Solids	PN1	K	K	K	PN1	N12	K	PN1	K	K	0.09%
W511	Absorbed Combustibles	PN1	P	PN1	PN1	PN1	N12	PN1	PN1	K	K	0.29%
W512	Paint & Residues	PN1	K	PN13	PN1	N5	N12	PN1	PN1	PN1	K	0.09%
W513	Resins	PN1	K	D	PN1	N5	N12	P	PN1	P	P	0.01%
W514	Animal Carcasses	PN1	P	K	K	PN1	N12	PN1	PN1	K	N5	0.00%
W520	Dry Organic Solids	PN1	K	PN1	PN1	PN1	N12	PN1	PN1	K	K	6.03%
W522	Plastic & Rubber	PN1	P	PN1	K	N5	N12	P	P	K	K	0.06%
W523	Paper, Cloth & Rags	PN1	P	N1	K	PN1	N12	PN1	PN1	K	K	2.50%
W524	Heavy Sludges & Asphalt	PN1	K	PN1	K	N5	N12	K	K	K	K	0.10%
W525	Graphite and Carbon	PN1	K	PN1	PN1	P	N12	K	K	PN1	K	1.48%
Subtotal												10.67%

Table 7.1. Preliminary evaluation of FWF for specific LLMW streams (cont.)

Code Number	Mixed Waste Category	Glass		Hydraulic Cement	Sulfur Polymer Cement	Ceramics		Organic Binders				% of Total WS
		Melter	Plasma Arc Furnace			Crystalline	Chemically Bonded	Thermoplastic Polyethylene	Thermoplastic Bitumen	Polyesters	Thermosetting Epoxy	
W600	Heterogeneous Wastes	PN13	P	PN13	PN13	N2	N12	PN13	N2	N2	N2	0.06%
W610	Construction, Cleanup, Process Debris	PN13	P	N2	K	N2	N12	N2	N2	N2	N2	5.71%
W620	Lab Packs	PN13	K	K	K	N2	N12	K	K	K	K	0.24%
W630	Equipment and Gloveboxes	N2	PN3	P	N2	N2	N12	N2	N2	N2	N2	0.02%
W640	Filters	PN57/3	K	K	K	N2	N12	K	K	P	K	1.81%
W650	Reactor Equip., Exp. Hardware, Fuel	N2	PN3	P	N2	N2	N12	N2	N1	N1	N2	0.98%
W660	Other Toxic Metal Containing Materials	N2	PN5	K	K	N2	K	K	K	K	N23	0.15%
W670	Lead Containing Components and Materials	PN1	PN5	PN15	PN15	N2	N12	P	N14	N14	N3	0.01%
W680	Hg Contaminated Materials	PN5	PN5	PN15	PN15	N5	N12	PN15	N4	K	N23	0.29%
Subtotal												9.26%
W700	Potential Problem Wastes											
W710	Tritium Wastes	N4	PN5	PN4	K	N2	K	N2	N4	K	N2	6.66%
W720	Pyrophorics	PN1/4	PN1	N	N	N5	K	K	N1	N1	N1	0.01%
W730	Nitrated Rags and Filters	N2	N2	PN3	N1	N2	N12	N2	N2	N2	N2	0.01%
W750	Compressed Gases	N2	N2	N2	N2	N2	N2	N2	N2	N2	N2	0.06%
W760	Beryllium Wastes	N2	P2	K	K	PN134	K	K	N1	N1	N1	0.01%
W770	PCB Contaminated	PN4/5	PN5	PN1	PN15	N2	N2	PN1	K	K	K	3.80%
Subtotal												10.34%
Total all Categories												100.00%

EVALUATION CRITERIA

D: FWF has been (must meet all 4 criteria)

1. Demonstrated (extensive documented testing) on components of this type of W8
2. Found to be effective (i.e., high waste loadings, minor pre-processing required)
3. Small fraction of original volume in the secondary WS
4. Documented as passing TCLP tests for at least some hazardous material

P: FWF has (must meet all 3 criteria)

1. Potential (some documented testing) for at least some hazardous material
2. Potential to be effective (i.e., high waste loadings, minor pre-processing required)
3. Potential for a small fraction of original volume in secondary WS.

PNX: FWF has been demonstrated (or is potentially) effective, but will require significant pre-processing or has other disadvantages, where 'X' is one of the following:

1. Thermal destruction
2. Evaporation
3. Major sorting/shredding
4. Major characterization (>4 hrs lab turnaround)
5. High volume in secondary waste stream
6. Precipitation/waste water treatment
7. Chemical destruction

K: FWF has not been tested and it is not known how effective it will be on the WS. (K(As) means TCLP testing with arsenic is the only question.)

NX: FWF will not be effective for one or more of the following, where 'X' is

1. Low waste loading
2. Significant pre-processing required
3. Poor TCLP test results
4. High volume in secondary WS
5. Volume of WS too low to warrant FWF development

NOTE: The evaluation was based on the feasibility of meeting both the technical requirements of a technology and the applicable regulatory requirements.

- Mercury (W430, W680, and W180) is particularly difficult to capture because of its high volatility. In LLMW streams, mercury is found as a contaminant in aqueous and organic liquids, as a liquid metal, and/or as a contaminant in solids. Table 6.1 indicates FWFs that may be effective in containing mercury contamination. SPC is the most likely FWF candidate because sulfur is the BDAT for emulsion of mercury; however, chemically-bonded ceramics and polyesters are also candidate FWFs. If the LLMW contaminated with mercury is a heterogeneous waste stream, an incineration process may be needed for volume reduction, with one of the above-mentioned FWFs as a treatment for the resulting offgas.
- Metal wastes (W400) are, from a regulatory standpoint, difficult to stabilize. An effective and preferred method for dealing with the radioactive and hazardous components of metal wastes may be to decontaminate the metal and then treat the secondary waste stream. As an alternative to this, a glass FWF resulting from a plasma arc process or a metal melter should be considered. Either of these processes will destroy organic contaminants and immobilize the toxic metals within the metal waste form that is not volatilized into the offgas system.
- Because of the large sizes of heterogeneous waste (W600) and the difficulties in size-reducing the waste, this waste stream is difficult to process. Like metal waste, an effective method for dealing with these waste may be decontamination. Also like metal wastes, alternative candidates for treating this waste stream are plasma arc processing and metal melting.
- Special wastes (W700) are those for which there are no demonstrated FWFs. Because tritium (W710) is difficult to capture in an offgas system, PCC and polyester FWFs are the most likely options for tritium-contaminated waste streams; both of these FWFs can accommodate water without evaporation. Pyrophorics (W720) and beryllium wastes (W760) can be treated with chemically-bonded ceramics. An alternate treatment is to oxidize the pyrophorics in small, safe quantities and then treat the remaining ash. The small amount of this waste makes this a potentially viable alternative. Nitrated rags and filters (W730) are "problem" wastes because of the potential for nitrocellulose, which is highly explosive. Chemical or thermal oxidation may be considered if it can be accomplished safely. Another option for this waste stream may be PCC using ice water, but this option requires a comprehensive evaluation. Compressed gases (W750) will need to be decompressed, perhaps in an autoclave; this waste stream would then become just a metal waste.
- Chlorine (W220) and nitrates (W321) are difficult to treat. It needs to be determined whether pre-treatment removal or post-treatment from the offgas system is the most effective means to immobilize chlorine and nitrates.

From these conclusions, it is apparent that research and development related to FWFs need to be directed to specific waste streams. Recommendations for achieving this are presented in Section 8.0.

8. RECOMMENDATIONS

The recommendations presented below were derived by the FWF TASR Working Group, and are those which were deemed by the FWF TASR Working Group as those needed that were a priority. These are identified as pressing issues facing FWF selection and evaluation. The recommendations have been divided into three sections: general recommendations, glass waste forms resulting from vitrification processes recommendations, and other FWF recommendations. For a complete listing of needs for each FWF, see Section 6 on Gaps and Deficiencies.

8.1 GENERAL RECOMMENDATIONS

The recommendations listed below are those that are not specific to FWF options. These issues need to be resolved prior to conducting significant work on individual FWFs, as the resolutions to these general issues will guide the efforts needed on individual FWFs.

Formulate Surrogate Wastes. Develop a list of specific formulations of surrogate wastes that represent the DOE's MWTP waste streams. These surrogate wastes would consolidate the 51 waste streams defined by the MWTP into a smaller, manageable number of waste streams that would include the expected worst-case conditions for levels of hazardous constituents. This is needed to conduct treatability studies for FWF options and to define the input required to develop a systems-analysis.

Define Input Requirements. Define the preliminary input requirements to each of the unit operations of the systems-analysis, and then define the preliminary output of each unit operation.

Develop Systems-Analysis. Develop a systems approach to analyzing and evaluating FWF requirements. The systems chosen should be consistent with DOE's strategy for the treatment of waste (i.e., site treatment, regional treatment). Specifically, the treatment of secondary waste streams must be included in the systems-analysis, as must site-specific performance assessments in the event that national or regional treatment and disposal facilities become available.

Develop Compositional Database. Develop a compositional database for newly-generated waste.

8.2 WASTE FORM PERFORMANCE ASSESSMENT

Define Environmental Factors. Define the major environmental factors that will effect FWF durability in disposal scenarios.

Determine Source Terms. Develop an approach for determining long-term waste form source terms. Provide leach data for generic PA (arid and non-arid).

Develop Monitoring Program. Develop a field monitoring program to validate models used in a PA.

Develop Screening Guidelines. Develop guidelines for screening which FWFs should be selected for the MWTP waste streams.

Establish Waste Loading Limits. Establish waste loading limits and toxic metal concentrations limits for which a FWF will pass the TCLP test.

Develop Certified Analytical Laboratory. Consider development of a central or regional EPA-certified analytical laboratory for characterization of waste.

8.3 GLASS WASTE FORMS FROM VITRIFICATION PROCESSES

In recognition of the fact that MWIP is considering the enhanced (glass) waste form as a preferred alternative to cement as a FWF, glass melting and plasma arc processing are paths that will need further research and development. Recommendations for each of these are presented below.

8.3.1 Glass Melter Processing

Conduct Crucible Melts. Conduct a series of crucible melts from a surrogate LLMW stream which represents significant portions of the expected DOE LLMW streams. The batch raw materials, melt mixing, and melt redox should be controlled. Volatility of components should be measured during the melting process. Resulting glass samples should be characterized for homogeneity, metal precipitation, and phase separation. In some cases, metal precipitation may influence the leach resistance of the glass waste form. Samples should be tested under site-specific waste storage conditions.

Determine Most Effective Glass Melting Method. Based on the wide variety of melter technologies available, determine the most effective method for melting glass for DOE LLMW streams.

Control Redox Conditions and Characterize Offgas. Test, on a pilot-scale, the most promising glass waste forms. Control the redox conditions in the melt, characterize the offgas, and characterize glass waste samples.

Test Glass FWF. Test the glass FWF under a wide variety of waste stream compositions and storage environments. These should include varying levels of hazardous constituents, testing for interactions between additions, varying melt parameters, and testing under typical storage conditions.

Establish RAM. Establish the reliability, availability, and maintainability (RAM) of various available glass melters.

Determine Toxic Metal Volatility. Determine the volatility of toxic metals under various redox conditions, with various vitrification technologies. Identify the chemical compounds formed in the offgas system. This information will provide an initial basis for selecting types of vitrification technologies and materials. This information will also assist in the development of offgas systems.

Establish Benchmark Glass. Establish a benchmark glass for LLMW similar to the benchmark glass which is being employed in the high-level program as a limit for leach resistance.

Establish Design Scale-Up Factor. Establish a design scale-up factor for the phased development of glass melters.

8.3.2 Plasma Arc Processing

Glass resulting from plasma arc processing, specifically, was not considered separately from glass FWFs in this report. However, when processing specific waste streams, plasma arc melting is radically different from more conventional glass melting and, therefore, the recommendations listed below are different than those described above for glass melters.

Determine Toxic Metal Volatilization. Determine the volatilization of toxic metals, the amount gas loading on an offgas system, and measure the destruction of organics.

Determine Compliance with TCLP. Determine whether a plasma arc glass product can pass the TCLP with metal wastes (W400, W420). Also, determine whether a plasma arc glass product can pass the TCLP test with organic solids such as absorbed combustibles (W511), animal carcasses (W514), plastic and rubber (W522), and paper, cloth, and rags (W523).

Determine Effectiveness on Heterogeneous Waste. Determine the effectiveness of plasma arc processing on heterogeneous waste (W600), including construction and demolition wastes (W610).

Assess Further Processing Needs. Assess the need of further processing of a FWF from a plasma arc process in order to meet FWF performance criteria.

8.4 OTHER FWF OPTIONS

The following recommendations for other FWF options provide a logical path for determining which FWF options should be used as backups or alternatives to glass.

8.4.1 Hydraulic Cement (PCC)

Determine Effectiveness on Tritium Wastes. Determine if polymer modified cement is effective for immobilization of tritium wastes (W710).

Determine Durability of Waste Grouts, Cements, and Concretes. Determine the general durability of waste grouts, cements, and concretes as LLMW forms. Develop a model that will predict waste retention life times for radioactive and hazardous constituents for differing disposal scenarios.

8.4.2 Sulfur Polymer Cement

Determine Effectiveness on Mercury Wastes. Determine the effectiveness of using SPC for solidification of liquid mercury and mercury-contaminated waste.

Determine Effectiveness on Chlorides. Determine the effectiveness of SPC in stabilizing salt cakes (chlorides) (W314).

Demonstrate Encapsulation at Production Scale. Demonstrate SPC encapsulation on DOE LLMW at production scale to confirm bench-scale processing and performance data.

Determine Long-Term Durability. Determine the long-term durability of SPC.

8.4.3 Crystalline Ceramics

Determine Necessary Particle Size Reduction. Determine the degree of particle size reduction necessary to produce acceptable ceramic waste forms using representative waste streams.

Determine Sensitivity to Waste Stream Variations. Determine the sensitivity of ceramic waste form properties to variation in waste stream composition for representative waste streams.

8.3.4 Chemically-Bonded Ceramics

Determine Effectiveness on Mercury Wastes. Determine whether chemically-bonded ceramics can be used as a FWF with mercury-contaminated aqueous liquids (W180) and liquid mercury (W430).

Determine Effectiveness on Salt Cakes and Processing Salts. Determine if chemical bonding of salt cakes (W314) and processing salts (W321) can produce an acceptable ceramic form.

Determine Effectiveness on Toxic-Metal-Containing Materials. Determine whether toxic-metal-containing materials (W660) can be formed into a ceramic.

Determine Effectiveness on Pyrophorics. Determine if pyrophorics (W720, W760) can safely chemically react with chemically-bonded ceramics.

8.4.5 Organic Binders

Thermoplastics

Confirm Uses of Polyethylene and Bitumen. Polyethylene has been developed for use with sludges and filter cakes (W311) and salt cakes (W314). Bitumen is well-suited for dry inorganic solids (W320). Confirmation is needed using actual or surrogate waste streams.

Determine Polyethylene's Effectiveness on Plastic, Rubber, and Lead-Containing Materials. Determine if plastic and rubber (W522) and lead-containing materials (W670) can be encapsulated in polyethylene without incineration and still pass the TCLP test and other performance criteria.

Demonstrate Polyethylene's Effectiveness at Production-Scale. Demonstrate polyethylene encapsulation of DOE's LLMW at production-scale to confirm bench-scale processing and performance data.

Determine Applicability of Bitumen for Aqueous Liquids, Corrosive Acids, and TC Metals. Further development and performance assessments are needed to verify the applicability of bitumen for waste streams such as aqueous liquids (W100), corrosive acids (W110), and TC metals (W150).

Thermosetting Organic Binders

Determine Epoxy's Effectiveness on Processing Salts. Determine if epoxy can solidify processing salts (W321) effectively, including passing the TCLP for toxic metals.

Determine Polyester's Effectiveness on Liquid Mercury and Resins. Determine the effectiveness of using polyester to encapsulate liquid mercury (W430) and resins (W513).

Determine Polyester's Effectiveness on Tritium Wastes. Determine if tritium waste (W710) can be stabilized with polyesters.

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