**Vitrification Treatment Options for
Disposal of Greater-Than-Class-C
Low-Level Waste in a Deep
Geologic Repository**

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Vitrification Treatment Options for Disposal of Greater-Than-Class-C Low-Level Waste in a Deep Geologic Repository

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ABSTRACT

The Department of Energy (DOE), in keeping with their responsibility under Public Law 99-240, the Low-Level Radioactive Waste Policy Amendments Act of 1985, is investigating several disposal options for greater-than-Class C low-level waste (GTCC LLW), including emplacement in a deep geologic repository. At the present time vitrification, namely borosilicate glass, is the standard waste form assumed for high-level waste accepted into the Civilian Radioactive Waste Management System. This report supports DOE's investigation of the deep geologic disposal option by comparing the vitrification treatments that are able to convert those GTCC LLWs that are inherently migratory into stable waste forms acceptable for disposal in a deep geologic repository.

Eight vitrification treatments that utilize glass, glass ceramic, or basalt waste form matrices are identified. Six of these are discussed in detail, stating the advantages and limitations of each relative to their ability to immobilize GTCC LLW. The report concludes that the waste form most likely to provide the best composite of performance characteristics for GTCC process waste is Iron Enriched Basalt 4 (IEB4).

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Vitrification Treatment Options for Disposal of Greater-Than-Class-C Low-Level Waste in a Deep Geologic Repository

1. INTRODUCTION

Commercially generated waste that is not acceptable for near-surface disposal under the U.S. Code of Federal Regulations, 10 CFR 61, is waste for which form and disposal methods must be different, and usually more stringent, than those specified by the Nuclear Regulatory Commission (NRC) for Class C waste. Unless otherwise approved by the NRC such waste must be disposed of in a deep geologic repository as defined in 10 CFR 60. The Department of Energy (DOE), in keeping with their responsibility under Public Law 99-240, the Low-Level Radioactive Waste Policy Amendments Act (LLRWPA) of 1985, is investigating greater-than-Class C low-level waste (GTCC LLW) disposal options, including emplacement in a deep geologic repository. This report supports the deep geologic disposal option investigation by comparing the vitrification treatments that are able to convert those GTCC LLW that are inherently migratory into stable waste forms acceptable for disposal in a deep geologic repository.

GTCC LLW is described in Section 2. This section also discusses those wastes that will require stabilization prior to disposal. Wastes that are usually pre-treated to facilitate vitrification and those that cannot be subjected to any form of thermal treatment are specifically identified.

Waste form criteria for disposal, as published by the Yucca Mountain Project Office, are listed in Section 3. Because there are no deep geologic disposal waste acceptance criteria for GTCC LLW, these waste form criteria serve to illustrate what may be expected. All waste form matrices discussed in this report meet or exceed these criteria.

Eight vitrification treatments are identified in Section 4; improved process development for six of these is ongoing. Product performance characteristics discussed in this section are the basis for a preferred waste form matrix. The vitrified waste form most likely to provide the best composite of performance characteristics for GTCC process waste is identified in this section. A general discussion supporting the rationale for preferring this waste form matrix is also given.

Conclusions and recommendations are stated in Section 5. Much is still to be determined regarding disposal options for GTCC LLW. It is entirely possible that vitrification itself is not the best disposal treatment for GTCC LLW.

References for information presented in this report are listed in Section 6. Quoted references, as well as those used to provide supplemental information, are listed.

A summary description of vitrification, its advantages and limitations, plus a brief introduction to glass matrix leaching mechanisms are given in Appendix A. Also included is an introduction to the principal glass melter technologies.

2. GTCC LLW DESCRIPTION AND ESTIMATED VOLUMES

Waste with constituent radionuclides listed in 10 CFR 61.55, Table 1 and Table 2, that exceed the Class C limits specified for those radionuclides, but is not high-level waste (HLW) as defined in 10 CFR 60, is classified as GTCC LLW. The radionuclides defining this classification and their respective Class C limits are stated in Table 1.

Table 1. NRC Class C limits for radionuclides (from 10 CFR 61.55, Tables 1 and 2).

Long-lived radionuclides	Concentration limits (Ci/m ³)	Half-life (yr)
¹⁴ C	8	5,730
¹⁴ C in activated metal	80	5,730
⁵⁹ Ni in activated metal	220	75,000
⁹⁴ Nb in activated metal	0.2	20,300
⁹⁹ Tc	3.0	211,000
¹²⁹ I	0.08	15,700,000
	Concentration limits (nCi/g)	
Alpha-emitting transuranic nuclides >5 year half-life	100	—
²⁴¹ Pu	3,500	14.35
²⁴² Cm	20,000	0.45
Short-lived radionuclides	Concentration limits (Ci/m ³)	
⁶³ Ni	700	100.1
⁶³ Ni in activated metal	7,000	100.1
⁹⁰ Sr	7,000	28.6
¹³⁷ Cs	4,600	30.2

GTCC LLW is generated as a result of commercial enterprise by NRC or Agreement State licensees. It is not "owned" or "generated" by any government agency, nor is it the result of atomic weapons production or military activities. For discussion in this report GTCC LLW is segregated into the following categories:

Commercial nuclear utility generated waste: Both activated metal and process wastes are generated during normal plant operations and during decommissioning.

Activated metal is composed of various nonfuel hardware components internal to the reactor. These components absorb neutrons, which causes certain constituent elements of the metal to become radioactive. The stainless steel fraction of this material could be melted and recycled to make waste disposal containers. The nonstainless steel portion, as well as the stainless steel fraction, if it is declared waste, will require physical sizing to accommodate the waste canister's dimensional configuration. This report assumes activated metals will not require vitrification for disposal as this waste form is inherently stable.

Process wastes include filters and decontamination resins, organic liquids, adsorbents contaminated with ^{14}C , and solids such as compactible trash, glass, plastic, contaminated metal scrap, lead, resins, filters, and lab equipment [Note: The filters in this waste generally use diatomaceous earth (SiO_2) and stainless steel screens]. This report assumes that utility-generated process wastes will require vitrification for disposal.

Sealed radiation sources: Sealed sources are typically small stainless steel capsules that contain high activity pelletized radioactive material. The radioactive material is generally double encapsulated, thereby ensuring a very stable waste form. A large number of capsules could be disposed of in a single waste container by mixing them with a polymer or concrete matrix. This monolithic mass would deter the sources from scattering should the waste container rupture. This report assumes that sealed sources will not require vitrification for disposal.

DOE-held commercial waste: Through contractual arrangements or for health and safety reasons, some commercially generated waste exceeding Class C limits is stored at DOE facilities. A DOE-ID legal counsel interpretation of the LLRWPA has tentatively determined that this waste does not require disposal as GTCC LLW in an NRC-licensed facility, as is required under Public Law 99-240. Such DOE-held waste is not addressed in this report.

Other generator: Except for utilities and sealed source users, this category encompasses all those involved with nuclear activities (e.g., ^{14}C manufacturers/users, industrial research/development firms, fuel fabrication/irradiation research labs, university research reactors, and sealed source manufacturers). In general terms, the waste from these diverse entities is comparable to utility process waste. However, there are differences; some of this waste, as shown in Table 2, qualifies as mixed waste under 40 CFR 261.21 (ignitable), 40 CFR 261.24 (toxic), and 40 CFR 261, Subpart D (listed). Note: All GTCC LLW generated by university research reactors is activated metals and, therefore, not included with

Table 2. "Other Generator" process waste.

Business type	Waste description	Hazard class	Nuclide
¹⁴ C users	Organic liquids, solidified waste, tritium, free liquid (25% water, 75% alcohols, acetone, hexane, xylene), solidified calcium carbonate, absorbed liquids, aromatics, salts, silica gel	40 CFR 261.21 40 CFR 261.24 40 CFR 261-D	¹⁴ C
Industrial R&D	Mixed oxide fuel pellets/rods	N/A	Pu, U
Burnup labs	Hot cell waste (fuel grinds, 25% compactible trash, glass, plastic, contaminated metal scrap, equipment/tools)	N/A	TRU, ⁶⁰ Co
Fuel fabricator	Decontamination waste (grit, sludge, filters) aqueous liquid	N/A	Pu, ²⁴¹ Am
Sealed source manufacturing	Absorbed liquids, compactible trash, filters, glass, lead, plastic, metal scrap, AmO ₂ /gold foil, scrap sources	40 CFR 261.24	²⁴¹ Am, ¹³⁷ Cs
Academic institution	Dry technetium salt	N/A	⁹⁹ Tc

Reference: EG&G Idaho, Inc., 1994.

the process waste as defined above. This report assumes that "Other Generator" waste will require vitrification for disposal.

Additional information about process wastes is given in the report *Greater-Than-Class C Low-Level Radioactive Waste Characterization: Estimated Volumes, Radionuclide Activities, and Other Characteristics* (EG&G Idaho, Inc., 1994). Data tables in Section 2 of the report state that the unpackaged volume of utility process waste will, by the year 2055, be 422 m³ with an activity of 923,016 Ci. Under Section 5 of the referenced report, the unpackaged volume of "Other Generator" waste will be 235 m³ with an activity of 12,680 Ci by year 2035, including 89 m³ of mixed waste. In total, 657 m³ of unpackaged process GTCC LLW will require disposal. (Note: The activity stated above includes all principal radionuclides present in the process waste: i.e., ¹⁴C, ⁶³Ni, ⁹⁰Sr, ⁵⁴Mn, ⁵⁵Fe, ⁶⁰Co, ⁶⁵Zn, ²⁴¹Pu, and TRU.) Assuming that a glass or glass-like waste form will be required for deep geologic disposal, process wastes from both the utility and "other generators" categories defined above will require vitrification for disposal.

Process waste includes some wastes of an organic nature and some containing ¹⁴C. Prior to vitrification, the organic waste is typically incinerated. Incineration reduces the gas generated in

the melter, which contributes to the transport of volatilized inorganics out of the melt. It also allows the volatilized organics to be collected at a lower temperature and more efficiently in a dedicated off-gas system.

Wastes, including organics, that contain ^{14}C (approximately 73 m³) should not be incinerated or vitrified. Such treatment would result in conversion of the ^{14}C to radioactive carbon dioxide gas that would be less suitable for disposal than the current waste form. Disposal options include encapsulating containers of ^{14}C waste in sulfur polymer cement, an encapsulation material that has passed NRC and Environmental Protection Agency (EPA) laboratory tests.

3. WASTE FORM CRITERIA FOR DISPOSAL

Although disposing of GTCC LLW in a deep geologic repository is an option, there is currently no approved plan to co-dispose GTCC LLW with spent fuel, HLW, or TRU waste. Also, at the present time there are no operational deep geologic repositories and, therefore, no approved disposal waste acceptance criteria (WAC) by which to judge the suitability of potential waste treatment technologies. In an attempt to identify possible disposal criteria the document entitled *Waste Acceptance Criteria for the Waste Isolation Pilot Plant* (DOE 1991) (WIPP WAC) was reviewed. Also, 10 CFR 60 and 61, DOE Order 5820.2A, and requirements documents published by the Yucca Mountain Project were all reviewed in depth. The WIPP WAC addresses only transuranic waste; GTCC LLW not only contains transuranic radionuclides but other radionuclides as well. 10 CFR 60 provides performance requirements for deep geologic disposal, not WAC. 10 CFR 61 is limited to near-surface disposal of classes A, B, and C LLW. DOE Order 5820.2A addresses government-generated waste for disposal in DOE-operated facilities, not in NRC-licensed facilities. The only information that has any, though limited, correlation to both the technical and institutional issues that define GTCC LLW is that information published by the Yucca Mountain Project.

The Yucca Mountain Project, currently in the early stages of evaluation, could become a DOE-operated, NRC-licensed facility for disposal of commercial and government-generated spent nuclear fuel and HLW. Although GTCC LLW may not need to satisfy the same disposal criteria as HLW, in a generic sense the studies, reports, and guidance published by the Yucca Mountain Project serve as a model and resource for other investigations addressing deep geologic disposal concerns. One such document, published by the Office of Civilian Radioactive Waste Management, is entitled *Waste Acceptance-System Requirements Document* (DOE 1994) (WA-SRD). It describes the functions to be performed and the technical criteria for a system to accept spent nuclear fuel and HLW into the Civilian Radioactive Waste Management System for disposal in a deep geologic repository.

3.1 Waste Form Criteria

The WA-SRD defines waste form as "the radioactive waste material and any encapsulating or stabilizing matrix." To qualify as a "standard waste form" under the WA-SRD, the waste form must satisfy the following criteria:

1. The waste form must be a solid. Particulate and fines must be immobilized in a monolithic mass.
2. Combustible waste must be reduced to a noncombustible form unless it can be demonstrated that such waste will not have any detrimental affect if ignited.
3. Free liquids, if any, must not result in spillage and spread of contamination should the waste container (canister) fail.
4. The waste must not contain explosives, pyrophoric, or chemically reactive materials in an amount that could compromise the repository's performance objectives.

5. The waste form must ensure criticality safety under normal and accident conditions.
6. The waste form must not initiate or contribute to internal corrosion that would lead to canister failure.
7. The chemical composition and the crystalline phase projections of the waste form must be known.
8. Elements present in concentrations greater than 0.5% by weight must be identified. The oxide composition of the waste form resulting from these elements must be known.
9. Radionuclides that have half-lives longer than 10 years and that are, or will be, present in concentrations greater than 0.05% of the total radioactive inventory (in curies) must be known for each canister of waste.
10. The mixed waste status of the waste form must be identified either by the generator for listed hazardous materials (40 CFR 261-D), or by testing for those characteristics specified in 40 CFR 261-C.

3.2 Canistered Waste Criteria

The "standard canistered HLW form" is borosilicate glass (glass containing 20 to 40 wt.% waste oxides, 40 to 65 wt.% silica, 5 to 10 wt.% boron oxide, and 10 to 20 wt.% alkali oxides, plus other oxide constituents) sealed inside an austenitic stainless steel canister 3 meters (~10 feet) long by 61 centimeters (24 inches) in diameter. The canistered waste must meet the following waste form dependent criteria:

1. Total heat generation must not exceed 1,500 watts at year of shipment.
2. Temperature must not exceed 400°C (752°F) during storage.
3. Free gas other than air, cover, and radiogenic gases must not be present after canister closure.
4. Detectable amounts of organic materials must not be present.

All the vitrified waste form matrices described in Section 4 of this report meet or exceed the WA-SRD "standard waste form" and "canistered waste criteria" stated above.

4. VITRIFIED WASTE FORM MATRICES

4.1 General Discussion

Vitrification (described in Appendix A) produces a waste form matrix that is generally very stable chemically, thermally, and mechanically. These matrices impede radionuclide migration by incorporating the waste into the matrix at the microstructural composition level. Long-term (several thousands of years) containment is accomplished by a combination of encapsulation and chemical bonding. The EPA has declared vitrification a treatment standard for mixed HLW (40 CFR 268.42).

Some waste form matrices are glass. They are an amorphous, rigid, noncrystalline structure of relatively low porosity. The glass product is composed primarily of silica, alumina, and oxides of alkali and alkaline earth elements. What distinguishes glass from crystalline structures is the lack of a definite melting point. When glass is heated to high enough temperatures, it will gradually deform and eventually form a viscous liquid. Glass products investigated as possible waste form matrices are described below; their characteristics are compared in Table 3 (Mayberry and DeWitt 1993 and Eddy et al. 1992).

Borosilicate glass (BSG) was the first glass formulated for use in radionuclide waste disposal. The boron (9–22%) is used to lower the melt viscosity and the melt temperature to below 1,150°C and to increase waste solubility. To some extent alumina (1–10%) also aids in reducing the viscosity and temperature, which is required because at higher temperatures (i.e., the melting point of iron, 1,538°C) BSG is extremely corrosive to the melter. Therefore, to use this technology for GTCC process waste, extensive sorting and sampling would be required to remove the metals. BSG has been demonstrated to have a low leachability rate and good overall product characteristics, making BSG the standard by which other glass or ceramic waste form matrices are evaluated. Treatable wastes include combustion ash, noncombustibles, and most soils.

Aluminosilicate glasses have excellent chemical, thermal, and mechanical durability. The disadvantages are the high melting temperatures. Melt corrosiveness is higher than for BSG. While the product characteristics are superior to BSG, the aluminosilicate glasses are more difficult to process. Treatable wastes include those stated for BSG plus basaltic soil and metallic aluminum.

The following two glass technologies, pyrex glass and phosphate glass, are well developed for commercial applications, but have demonstrated high corrosive characteristics in the melter when they are used as waste form matrices. They are included in this report for information only and not considered viable waste form matrices for GTCC process waste.

Pyrex glass is comparable to BSG in performance except for a lower waste loading capability. When formulated as a waste form matrix, it requires much higher process temperatures, resulting in melter corrosion comparable to aluminosilicate glass. Given that the waste loading is less than BSG and melter corrosion is more problematic, pyrex glass is not currently being used as a waste glass.

Table 3. Vitrified product performance characteristics (Kong et al. 1992).

Product characteristics	Desired performance	BSG	ASG	GC	SR	IEB	IEB4
Chemical stability leachability	High leach resistance for radionuclides and toxic metals ^a	G	G	G	E	G	E
	High resistance to chemical changes from reactions	E	G	E	E	E	E
Thermal stability	Resistance to radiation thermal damage	G	E	E	E	E	E
	Resistance to geothermal induced changes	G	E	E	E	E	E
Mechanical durability	Impact resistance against generation of cracks and fines	G	E	E	E	E	E
Macroscopic homogeneity	Properties performance and certification	G	E	E	E	E	E
	Accommodate heterogeneous waste materials	P	G	G	E	E	E
	Uniform distribution of radionuclides	G	E	E	E	E	E
Environmental compatibility	Stability must be comparable to natural analog	E	E	E	E	E	E
	Public acceptance	E	E	E	E	E	E
Waste loading	High retention of radionuclides identified in 10 CFR 61	G	E	G	E	E	E
	High metal dissolution	P	G	G	U	E	E
	High waste volume reduction	P	G	G	E	E	E

a. Method 1311 Toxicity Characteristic Leaching Procedure (TCLP) stated in 40 CFR 261 Appendix II shall be used to determine leachability.

Legend:

BSG = borosilicate glass, ASG = aluminosilicate glass, GC = glass ceramic, SR = synroc,
IEB = iron enriched basalt, IEB4 = iron enriched basalt with zirconium and titanium added.

E = Excellent, G = Good, A = Acceptable, P = Poor, N = not acceptable, U = unknown

Phosphate glasses are durable, but they are highly corrosive to the melter, have poor thermal stability above 550°C, and have low waste solubility. Research work on phosphate glass as a waste form matrix has been abandoned.

A synthetic material, **glass ceramic**, can be produced as a silicate-titanate or silicate-phosphate waste form matrix. This product, having excellent chemical, thermal, and mechanical durability, is superior to BSG. However, being a crystalline structure, it is more difficult to process and not as forgiving as BSG with variations in waste composition. In particular, alkali content should be kept to a minimum; alkali metals or alkali earth compounds decrease the viscosity of the melt and, if allowed to reach an intergranular glass phase, increase leachability of the waste form matrix. Using a glass ceramic matrix requires tailoring the dissolution of the waste in a number of mineral phases. Additives are used to alter the waste composition, thus tailoring the wastes chemically to the radionuclides. Treatable wastes include those stated for BSG plus basaltic soil and metallic aluminum. The EPA has identified glass ceramic as the best demonstrated available technology (BDAT) for HLW that has been calcined (57 Federal Register 22046).

A synthetic three-phase crystalline titanate called **Synroc** can incorporate 10–20% of all HLW components into solid solution. There is no information available for other waste types; however, chemical stability should be similar for GTCC process wastes. Synroc is very leach resistant up to 300°C. The process requires mixing and calcining the waste with a well controlled composition of titanium, zirconium, aluminum, boron, and calcium oxide. The calcined products are then consolidated by hot-pressing to a high density waste form at a temperature well below the melting temperature. Treatable wastes include those stated for BSG plus basaltic soil, metallic aluminum, zircon sand, and titanate sand. It may be possible to include metallic iron if the process temperature is >1500°C.

Iron enriched basalt (IEB), an analog to natural basaltic rock, has a silica composition of 35–57% and iron oxide of 10–35%, with relatively low (<10%) alkali metals concentrations. Heavy metal oxides can be immobilized in a slag that has excellent durability. When IEB is cooled slowly, crystals very similar to Synroc are formed. The leach resistance of IEB (and IEB4 discussed below), as demonstrated for uranium and americium-241, is superior to borosilicate glass. The principal reason for this increased leach resistance is depletion of high leach rate elements (vitreous alkali constituents) as the crystalline structure is developed, thereby increasing the proportion of low leach rate elements such as silica and alumina. A wide range of TRU waste forms, such as cemented sludge, organics, cemented organics, evaporator salts, and stainless steel metals, were examined in an IEB melter. If the silica content is increased by adding soil (>60 wt.%) to these waste streams, the ratio of metal (iron oxide) to silica can be adjusted to match desired IEB characteristics without removing the metal pieces or other feed waste constituents. An exception is evaporator salts; having a high alkaline content, they tend to increase leachability. If more than 70% soil is added to the feed waste, the waste form volume increases and its composition approaches that of a ceramic rather than IEB. Treatable wastes include those stated for BSG plus basaltic soil, metallic aluminum, zircon sand, titanate sand, and metallic iron.

Iron enriched basalt 4 (IEB4) is similar to IEB except that zirconium and titanium, both Group IVB elements, are added. Zirconium itself has a high solubility for uranium oxide, while

the titanium combined with zirconium acts as a scavenger for both TRU (e.g., plutonium) and TRU surrogate radionuclides. If the melt temperature is held in a range where the zirconium-titanium based crystals remain in suspension, these crystals will scavenge thorium, uranium, TRUs, activation products, and fission products from the melt. Leach rates are approximately an order of magnitude lower than those obtained for a typical borosilicate glass when 30-50 wt.% soil (50-70% waste loading) is added to the IEB4. The IEB4 product could well surpass IEB and Synroc for treating TRU waste. Treatable wastes include those stated for BSG plus basaltic soil, metallic aluminum, zircon sand, titanate sand, and metallic iron.

4.2 Preferred Waste Form Matrix

The best vitrified product is produced by a feed waste that is homogeneous and has been well characterized chemically. As an example, the DOE BSG processes at both West Valley, New York, and the Savannah River Site in South Carolina accept feed waste as homogeneous radioactive sludge or slurry with known chemical characteristics. Additives, collectively known as "frit," are formulated to match the feed waste characteristics to those of the BSG. The performance characteristics of the glass produced are highly dependent on the chemical compatibility between the feed waste/frit mixture and the glass. Therefore, the feed waste/frit mixture is processed by the melter in batches, with each batch being sampled and chemically modified just prior to being vitrified.

The waste form discussion in this section is based on studies and technologies developed for HLW, not GTCC process waste. These studies suggest that vitrified waste forms vary considerably in their tolerance to accept feed wastes with discrete constituents. Also, the melter technology employed has a major affect on the ability to vitrify these wastes. In depth studies comparing the interactive performance of the principal variables (feed wastes, melter technologies, and the resultant vitrified product) have not been published. Given that GTCC process wastes are not homogeneous, nor have they been chemically characterized, it is not possible to determine the BEST waste form matrix nor melter technology. However, the physical form (e.g., plastic, metal, resins, filters, combustibles, or noncombustibles) of GTCC process waste is known, as well as the radionuclides of concern and potential radioactivity. Conclusions from this information lead to a presumption of the chemical characteristics that could be expected and how they may react when vitrified. If one waste form matrix is desired to immobilize all GTCC process waste (^{14}C , and free liquids excepted), IEB4 produced in a plasma-arc melter offers the best composite of performance characteristics.

The IEB4 product does not require that the waste be sorted before vitrifying. The single advantage of IEB4 over IEB is the ability to immobilize plutonium and uranium. Both IEB and IEB4 have demonstrated leach resistance and waste loading factors higher than BSG or the other waste form matrices discussed in this report. IEB/IEB4 can also easily process metallic iron by formulating a frit composed of silica and aluminum, possibly contaminated soil. If desired, the metal can be drawn off the melt and recycled. Another advantage of adding soil is that it counteracts high concentrations of alkali nitrates that tend to make the waste form matrix less leach resistant.

Off-gas production, collection, and processing problems are common to all vitrification treatment melters. Gases generated by combustibles travel to the surface of the melt entraining

those volatile contaminated inorganics (e.g., lead, ^{137}Cs , sulfur, and halogens) the process is attempting to immobilize. Also, by passing on to the off-gas system the added quantity of inorganics, increased off-gas collection and residue treatment capability is required. For ease of operation all six waste form treatments discussed in this report recommend incinerating combustibles prior to vitrification. However, state-of-the-art IEB/IEB4 melter technology investigations are exploring the possibility of volatilizing combustibles directly in the melter, making incineration unnecessary.

The preparation necessary to make each generator's GTCC process waste compatible with each of the six treatments is given Table 4. Free liquids and ^{14}C are unacceptable to all six treatments, and metals are unacceptable or sensitive to all treatments except IEB and IEB4. With these constituents excluded, and given that with current technology combustibles are incinerated as a prerequisite to vitrification, GTCC process waste could be immobilized in BSG or any of the other waste form matrices discussed in this report. For those waste forms or melter technologies requiring uniformity, the feed waste could be made homogeneous by shredding, grinding, incineration, mixing or a combination as part of a treatment train. The chemical composition of the homogeneous volume could then be determined and a frit formulated to permit vitrification.

Table 4. Pretreatments necessary to make each generator's GTCC process waste acceptable for vitrification.

Business type	BSG	ASG	Ceramic glass	Synroc	IEB	IEB4
¹⁴ C users	Not acceptable	Not acceptable	Not acceptable	Not acceptable	Not acceptable	Not acceptable
Industrial R&D ^a	Acceptable	Acceptable	Acceptable	Acceptable	Acceptable	Acceptable
Burnup labs ^b	Remove metals	Make homogeneous	Make homogeneous	Questionable for metals	Acceptable	Acceptable
Fuel fabricator ^c	Remove filters w/metal parts	Make homogeneous	Make homogeneous	Questionable for metals	Acceptable	Acceptable
Sealed source mfg. ^d	Remove metals	Make homogeneous	Make homogeneous	Questionable for metals	Acceptable	Acceptable
Academic institution ^e	Acceptable	Acceptable	Acceptable	Acceptable	Acceptable	Acceptable

Note: Baseline assumptions for this table are that all combustibles are incinerated and there are no free liquids.

a. All the waste forms will accept this waste. However, the plutonium and uranium content makes IEB4 the logical choice.

b. Synroc may be able to process metals if a plasma-arc or similar high-temperature melter is used. Studies to date have used joule-heated melters that operate at a lower temperature and do not tolerate metals in the melt. The preferred waste form matrix choice is IEB4 because of the plutonium and uranium fuel grinds in the waste.

c. The IEB4 waste form matrix is preferred because of the plutonium and uranium content in the waste.

d. Either IEB or IEB4 are preferred because of their ability to accept waste as is from the manufacturing process.

e. Technetium salts will immobilize in all six waste form matrices. The lower temperature for BSG may translate to lower overall process cost.

5. CONCLUSIONS AND RECOMMENDATIONS

1. With sorting and certain pretreatments it appears that GTCC process waste could be immobilized in BSG or any of the other waste form matrices discussed in this report.
2. All six vitrified waste form matrices described in this report meet or exceed the WA-SRD "standard waste form" and "canistered waste criteria" published by the Yucca Mountain Project Office.
3. Because of the lack of published studies specific to GTCC LLW, it is not possible to recommend the BEST waste form matrix nor melter technology for GTCC process waste. However, the one waste form matrix that appears able to immobilize the greatest variety of GTCC process waste (^{14}C , and free liquids excepted), is iron enriched basalt 4 (IEB4) produced in a plasma-arc melter.
4. Given the present state of the art, GTCC process waste containing organic constituents should be incinerated as a prerequisite to vitrification. Incineration reduces the gas generated in the melter, which contributes to the transport of volatilized inorganics out of the melt.
5. Wastes, including organics, that contain ^{14}C (approximately 73 m^3) should not be incinerated or vitrified. Such treatment would result in conversion of the ^{14}C to radioactive carbon dioxide gas that would be less suitable for disposal than the current waste form.
6. Although not addressed in this report, it is entirely possible that vitrification itself is not the best choice. When disposal requirements for GTCC LLW are known, the treatment options should be revisited.

6. REFERENCES

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Appendix A

Theory of Vitrification

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Theory of Vitrification

A summary description of the theory of vitrification, its advantages and limitations, plus a brief introduction to glass matrix leaching mechanisms are given in this appendix. Also included is an introduction to the principal glass melter technologies.

VITRIFICATION

Vitrification is the process of converting materials into a glass or glass-like substance, typically by employing a thermal process. (Note: vapor deposition, solution hydrolysis, and gel formation processes can form glassy materials without heat.) For radioactive and hazardous waste, vitrification using a thermal process is desirable because (a) organic contaminants are destroyed by pyrolysis (oxygen-lean burn) or combustion (oxygen-rich burn) and (b) inorganics are stabilized by incorporating them via covalent or ionic bonding into the structural composition of the glass or by encapsulating them in the product glass.

Most glasses used for waste immobilization are silicate glasses. They are composed primarily of silica, alumina, and oxides of alkali and alkaline earth elements. There are many materials that contain adequate quantities of these raw ingredients; when heated, the ingredients interact to form the structural composition that is glass. Any contaminants present in these materials are immobilized by chemical bonding within the glass structure. However, not all materials identified as waste contain the proper ratio of ingredients to make glass directly. As shown in Table A-1, the composition of the feed waste directly affects the processing parameters and waste form matrix performance. To create the desired performance, custom formulated additives known collectively as "frit" are used. Adjusting frit composition facilitates tailoring the waste form matrix to meet performance requirements.

Advantages and Disadvantages

The primary advantage of vitrification over other treatments is durability. Many waste glass formulations perform very well in leach tests, thus indicating high chemical bonding. They have also shown high physical integrity and perform well even when devitrified (crystallized). Further, some estimates and comparisons with natural analogs indicate that waste glasses may exhibit these characteristics over geologic time.

Another advantage is the ability to incorporate a wide variety of contaminants and feed wastes without a significant decrease in quality. Various tests and studies (EPA 1992) indicate that vitrification should be investigated when evaluating treatments for many wastes including, but not limited to

Radioactive wastes and sludge, including those containing Resource Conservation and Recovery Act (RCRA) hazardous constituents are as amenable to the processing capabilities inherent with vitrification as nonradioactive waste and sludge. The presence of radioactivity

Table A-1. Affects of feed waste oxides on processing and waste form performance (EPA 1992).

Oxides	Processing	FWF performance
Silicon	Increases viscosity; reduces waste solubility	Increases durability
Boron	Reduces viscosity; increases waste solubility	Increases durability in low amounts, reduces in large amounts
Sodium	Reduces viscosity and resistivity;	Reduces durability
Lithium	Same as sodium; increases trend to devitrify	Reduces durability
Potassium	Same as sodium; decreases trend to devitrify	Reduces durability
Calcium	Increases then reduces viscosity and waste solution	Increases then reduces durability
Magnesium	Same as calcium; reduces trend to devitrify	Same as calcium
Titanium	Reduces viscosity; increases then reduces waste solubility; increases trend to devitrify	Increases durability
Zirconium	Reduces waste solubility	Increases durability
Aluminum	Increases viscosity and trend to devitrify	Increases durability
Iron	Reduces viscosity; hard to dissolve	Increases durability
Uranium	Reduces trend to devitrify	Reduces durability
Nickel	Increases trend to devitrify; hard to dissolve	Reduces durability
Manganese	Hard to dissolve	Increases durability
Zeolite	Slow to dissolve; produces foam	Increases durability
Sulfate	Antifoam, melting aid; increases corrosion	Too much causes foam, or soluble second phase

may dictate the use of shielding or containment systems in keeping with established nuclear industry practices.

Contaminated soils are amenable to vitrification because soils generally contain high percentages of silica, alumina, and other glass-forming raw materials.

Incinerator ashes, both bottom ash and fly ash are amenable to vitrification. Incineration significantly reduces the organic component and overall waste volume, but the inorganic contaminants remain. Vitrification, by serving as a follow-up treatment after incineration, can immobilize these inorganics.

Industrial wastes, such as paint sludge and metal-bearing sulfates, carbonates, and phosphates, are acceptable for vitrification. Transition metals, such as arsenic, barium, cadmium, chromium, and lead, can be vitrified if a suitable off-gas system is employed.

Medical wastes that are vitrified are free of disease-causing microorganisms, such as bacterium or fungus (pathogens), as well as having their radioactive constituents immobilized in the waste form matrix.

A major technical disadvantage is the need to limit gas generation and emissions and to minimize volatilizing inorganic contaminants during the melting phase. This is accomplished through control of various process parameters. In concert with process control is the need to remove contaminants from the evolved off-gas. Ceramic fiber filters, gas-to-water heat exchangers, water spray chambers, and charcoal and HEPA filters are some techniques employed in systems used to treat the off-gas.

Limitations

Although vitrification has wide application as a treatment for radioactive and hazardous waste, it does have limitations. The following conditions most limit the effectiveness of vitrification:

High feed waste moisture content, although not a technical limitation, increases the melter's operating cost because more time and energy are required to expel the water before the waste will vitrify. One alternative is preheating the waste to reduce its moisture content prior to melting.

Feed waste composition, by virtue of its chemical constituents, impacts the durability of the vitrified product. By using a batch process method, the feed waste can be sampled prior to the melting operation and suitable additives (frit) formulated to assure an acceptable glass product is produced.

Feed waste compatibility refers to the physical size, configuration, and composition of the waste relative to the process equipment's ability to handle, contain, and process it. Requirements imposed by the melter determine the extent and nature of feed waste preparation needed.

Combustible materials include solids, liquids, and packages with void spaces. Gas generation occurs as a result of pyrolysis, combustion, and intrusion of the molten glass into the void spaces, thereby releasing entrapped air. The main concern is that the generated gases can provide an important pathway for the movement of contaminated inorganics out of the melt by a mechanism called "carrier gas transport." If the feed waste includes a significant amount of combustible material, incineration prior to vitrification would be most beneficial.

Limiting materials in the feed waste, such as halogenated compounds, reducing agents, certain metals or high concentrations of metals, affect processing or product quality. Halogens such as fluorine and chlorine produce a porous product and may also corrode the melter if they evolve as off-gases. Reducing agents such as carbon and ferrous salts affect

bonding efficiencies, while metals such as mercury and cadmium resist incorporation into the melt, reduce product quality, and are easily volatilized. A pretreatment to reduce the concentration of limiting materials is recommended, or more frit could be added to dilute the feed waste.

Encapsulating pieces or particles of waste in a glass monolith protects such waste from chemical attack and inhibits their migration to the environment, assuming the glass does not fail as a result of chemical leaching or stress fracturing. The potential for stress fracturing may be increased by such encapsulation because of structural discontinuity or differences in thermal expansion coefficients. Because covalent or ionic bonding within the glass structure does not occur, the waste is free to leave the glass by any available pathway.

Waste Form Matrix Leachability

The single most important characteristic of waste glass is chemical immobilization, the ability to resist leaching the contaminants in the matrix when exposed to liquids. Without this characteristic the cost associated with vitrification would most likely not be justified compared with other treatment technologies.

Although generally considered to be inert, all vitreous materials are chemically active (subject to leaching) to some degree. There are two principal ways to attack vitrified materials, matrix dissolution and interdiffusion.

Matrix dissolution of most vitreous silicate materials is the result of exposure to alkaline solutions with pH values above 9. The process begins by hydrating the surface then dissolving the silica network. As the structure is destroyed, other constituents within the matrix are released. The dissolution rate is generally linear with time, but increases by a rate of 2 to 3 for each pH unit increase. It is also temperature reactive, increasing by a factor of 2 to 2.5 for each 10°C temperature rise. An exception, borosilicate glass, suffers matrix dissolution when exposed to acidic (below pH 5) liquids. The attack increases linearly with time and is very destructive.

Interdiffusion is an ion exchange process resulting from exposure to an acidic (below pH 5) liquid. It extracts elements present as network modifiers in exchange for hydronium ions in solution, leaving the silica structure almost intact. The rate of attack is proportional to the square root of time. It is also temperature reactive by a factor of 1.5 to 2 for each 10°C temperature rise. Network modifiers, such as beryllium, cobalt, lead, nickel, and strontium, can be extracted from the waste form matrix.

GLASS MELTER TECHNOLOGIES

Glass melter technologies are divided into two categories, those employing electricity to generate process heat and those using fossil fuels. Electrically heated melters can be designed to use joule, plasma, microwave, induction, or electric arc furnace heating principles. Fossil fuel heated melters use waste, fuel, or both to generate heat, generally in a rotary kiln incinerator.

In a **joule heated melter (JHM)**, an electric current flows through the material being melted. Because the material is resistant to electric current flow, the current loses power in the form of heat, which is dissipated in the material. The JHM process is affected by several glass properties:

- Solid glass is a poor electrical conductor (high resistance), but molten glass is a good conductor and can be heated directly by electric current. Because glass resistance decreases rapidly as the temperature increases, the melt is started by some form of pre-heating followed by joule heating when the glass is liquified.
- The alkali content of the glass is particularly important in carrying the charge in the glass melt. The more alkali, the lower the resistivity.
- Melt viscosity is the most important processing property; it controls processing rate, product homogeneity, convective mixing, and pouring by impacting the heat generated convection currents.
- An alternating current must be used to avoid electrolysis and anodization of electrodes.

JHMs can handle inert materials and a small amount of combustibles, but are susceptible to severe corrosion and oxidation at the high temperatures needed to melt metals or soil. Metals and soils should be avoided, and the combustible portion of the waste should be incinerated separately, with only the ash going to the melter.

Plasma heating relies on the conversion of a gas into a plasma (ionized gas) through the application of an electric arc. Because of the ionized nature of plasma, it can provide high operating temperatures and high power densities.

Plasma heating is characterized by using a "nontransferred" or a "transferred" arc process. The nontransferred arc process heats only by conduction, producing a dispersed heat needed for air and gas drying. With the transferred arc process the feed waste becomes one of the electrodes, thereby making it tolerant of variances in feed waste size and composition. Incinerator ash, soil, and medical wastes have been successfully treated. Because of the high temperatures involved, a disadvantage of arc/plasma-heated melters is vaporizing high vapor pressure metals.

In **microwave heating**, a form of dielectric heating, the feed waste absorbs electromagnetic radiation. The waste acts as a dielectric, or an electric insulator. Dielectric heating is classified by the frequencies used: between 10 and 300 MHz for radio frequency heating and between 900 and 30,000 MHz for microwave heating. Only microwave heating has been used to vitrify waste.

The main advantage of the microwave heating is that the heat is produced directly in the feed waste. A second advantage is power density. The main disadvantage is relatively high energy consumption. Another disadvantage is arcing that results from inducing currents in any metal pieces that may be in the waste. Because such arcing is damaging to the microwave generator, the waste must be pre-sorted to remove all metals. A microwave process at Rocky Flats has achieved ~55% waste loading using ash from incinerated waste. The product, borosilicate glass, easily meets all performance characteristics.

Induction heating is accomplished by inducing an eddy current in the waste material. One method is to use a solenoid to create a variable magnetic field inside the container. An electrically conductive body is placed inside the magnetic field; the variation in the magnetic field induces an electromotive force current (EMF) in the conductor. The EMF, in turn, generates eddy currents that are converted into heat in the waste from the joule effect. Calcined HLW is being treated in this manner.

Electric arc furnaces heat by creating current flow between two electrodes in an ionized gas environment. They differ from plasma processes in that a plasma is not created and, therefore, is not part of the heat transfer mechanism. Given this process was first developed for the metal industry, metal waste is easily melted.

A modification of the electric arc furnace has been developed that adds plasma heating to a direct-current electric arc to pyrolyze waste material in a sealed unit. Generated gases must pass through an electric arc and a plasma-heated zone, which effectively scrubs the offgas.

Thermal process heating is produced by burning waste, fuel, or both. Melting most commonly occurs in a rotary kiln operated in a slagging mode to produce glass. The rotating cylinder facilitates mixing wastes with combustion air, as well as promoting transfer of wastes through the kiln. Kiln incineration may be used as a vitrification process by itself or as an incinerator before vitrification in a treatment sequence.