Designation: C 1571 – 03

Standard Guide for Characterization of Radioactive and/or Hazardous Wastes for Thermal Treatment[1]

1. Scope

1.1 This guide identifies methods to determine the physical and chemical characteristics of radioactive and/or hazardous wastes before a waste is processed at high temperatures, for example, vitrification into a homogeneous glass ,glass-ceramic, or ceramic waste form. This includes waste forms produced by ex-situ vitrification (ESV), in-situ vitrification (ISV), slagging, plasma-arc, hot-isostatic pressing (HIP) and/or cold-pressing and sintering technologies. Note that this guide does not specifically address high temperature waste treatment by incineration but several of the analyses described in this guide may be useful diagnostic methods to determine incinerator off-gas composition and concentrations.

The characterization of the waste(s) recommended in this guide can be used to (*1*) choose and develop the appropriate thermal treatment methodology, (*2*) determine if waste pretreatment is needed prior to thermal treatment, (*3*) aid in development of thermal treatment process control, (*4*) develop surrogate waste formulations, (*5*) perform treatability studies, (*6*) determine processing regions (envelopes) of acceptable waste form composition, (*7*) perform pilot scale testing with actual or surrogate waste, and/or (*8*) determine the composition and concentrations of off-gas species for regulatory compliance.

The analyses discussed in this standard can be performed by a variety of techniques depending on equipment availability. For example, Gas Chromatograph Mass Spectrometry (GC/MS) can be used to measure the amount and type of off-gas species present. However, this standard assumes that such sophisticated equipment is unavailable for radioactive or hazardous waste service due to potential contamination of the equipment. The analyses recommended are, therefore, the simplest and least costly analyses that can be performed and still be considered adequate

1.2 This guide is applicable to radioactive and/or hazardous wastes including but not limited to, high-level wastes,[2] low-level wastes,[3] transuranic (TRU) wastes, hazardous wastes, mixed (hazardous and radioactive) wastes, heavy metal contaminated wastes, and naturally occurring or accelerator produced radioactive material (NARM or NORM) wastes. These wastes can be in the physical form of wet sludges, dried sludges, spent waste water filter aids, waste water filter cakes, incinerator ashes (wet or dry), incinerator blowdown (wet or dry), wastewaters, asbestos, resins, zeolites, soils, unset or unsatisfactory cementitious wastes forms in need of remediation, lead paint wastes, etc. and combinations of the above. This guide may not be applicable to piping, duct work, rubble, debris waste or wastes containing these components.

1.3 This guide references applicable test methods that can be used to characterize hazardous wastes, radioactive wastes, and heavy metal contaminated process wastes, waste forms, NARM or NORM wastes, and soils.

1.4 These test methods must be performed in accordance with all quality assurance requirements for acceptance of the data.

1.5 *This standard may involve hazardous materials, operations, and equipment. This standard does not purport to address all of the safety concerns, if any, associated with its use. It is the responsibility of the user of this standard to establish appropriate safety and health practices and determine the applicability of regulatory limitations prior to use.*

2. Referenced Documents

2.1 *ASTM Standards:*

C 92 Test Methods for Sieve Analysis and Water Content of Refractory Materials[4]
C 146 Test Methods for Chemical Analysis of Glass Sand[4]
C 162 Terminology of Glass and Glass Products[4]

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[1] This guide is under the jurisdiction of ASTM Committee C26 on Nuclear Fuel Cycle and is the direct responsibility of Subcommittee C26.07 on Waste Materials.

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[2] High level waste (HLW) is used as a generic term that includes high level liquid waste (HLLW) and high level radioactive waste (HRW).

[3] Low level waste (LLW) is used as a generic term that includes low level liquid waste (LLLW), low level radioactive waste (LLRW) and low activity waste (LAW).

[4] *Annual Book of ASTM Standards*, Vol 15.02.

C 169 Methods for Chemical Analysis of Soda-Lime and Borosilicate Glass[4]
C 242 Terminology of Ceramic Whitewares and Related Products[4]
C 859 Terminology Relating to Nuclear Materials[5]
C 1109 Test Methods for Analysis of Aqueous Leachates from Nuclear Waste Materials using Inductively Coupled Plasma-Atomic Emission Spectrometry[5]
C 1111 Test Method for Determining Elements in Waste Streams by Inductively Coupled Plasma-Atomic Emission Spectroscopy[5]
C 1168 Practice for Preparation and Dissolution of Plutonium Materials for Analysis[5]
C 1317 Practice for Dissolution of Silicate or Acid-Resistant Matrix Samples[5]
C 1463 Practice for Dissolving Glass Containing Radioactive and Mixed Waste for Chemical and Radiochemical Analysis[5]
D 1129 Terminology Relating to Water[6]
D 4327 Test Method for Anions in Water by Ion Chromatography[6]

2.2 *Other Documents:*

US EPA Standard SW846, Test Methods for Evaluating Solid Waste
Resource Conservation and Recovery Act (RCRA), 40CFR 240-271, November 21, 1976
DOE Methods for Evaluating Environmental and Waste Management Samples, March, 1993, DOE.EM-0089T, Rev. 1
Radioanalytical Technology for 10 CFR Part 61 and Other Selected Radionuclides, Literature Review, C. W. Thomas, V. W. Thomas, and D. E. Robertson, PNNL-9444, March, 1996

3. Terminology

3.1 *Definitions:*

3.1.1 *analysis (physical or chemical)*—the determination of physical or chemical properties or composition of a material. **C 859**

3.1.2 *byproduct material*—the tailings or wastes produced by the extraction or concentration of uranium or thorium from any ore processsed primarily for its source material content, including discrete surface wastes, resulting from uranium solution extraction processes. Underground ore bodies depleted by such solution extraction operations do not constitute "byproduct material." **10 CFR Part 40**

NOTE 1—A supplementary definition can be found in 10 CFR Part 20; any radioactive material (except special nuclear material) yielded in, or made radioactive by, exposure to the process of producing or utilizing special nuclear material.

3.1.3 *calcine*—to fire or heat a granular or particulate solid at less than, fusion temperature but sufficient to remove most of its chemically combined volatile matter (for example, H_2O, CO_2) and otherwise to develop the desired properties for use.[7]

3.1.4 *debris waste*—solid material exceeding a 60mm particle size that is intended for disposal and that is: a manufactured object; or plant or animal matter; or natural geologic material.[8]

3.1.5 *devitrification*—crystallization of glass. **C 162**

3.1.6 *drying*—removal by evaporation, of uncombined water or other volatile substances from a ceramic raw material or product, usually expedited by low-temperature heating. **C 242**

3.1.7 *geologic mill tailings*—common rock leftover from mining or oil well drilling operations that may contain hazardous or radioactive constituents, can include natural occurring radioactive material (NORM).

3.1.8 *glass ceramic*—solid material, partly crystalline and partly glass. **C 162**

3.1.9 *hazardous waste*—(*a*) in a broad sense, any substance or mixture of substances having properties capable of producing adverse effects on the health or safety of a human (see also RCRA hazardous waste); (*b*) any waste that is "listed" in 40CFR Parts 261.31-261.33 or exhibits one or more of the characteristics identified in 40CFR Parts 261.20–261.24, is a mixture of hazardous and nonhazardous waste, or is determined to be hazardous waste by the generator.

3.1.10 *heavy metal contaminated waste*—a common hazardous waste; can damage organisms at low concentrations and tends to accumulate in the food chain. Examples are lead, chromium, cadmium, and mercury.

3.1.11 *high-level liquid waste (HLLW)*—the radioactive aqueous waste resulting from the operation of the first cycle extraction system, or equivalent concentrated wastes from subsequent extraction cycles, or equivalent wastes from a process not using solvent extraction, in a facility for processing irradiated reactor fuels.

3.1.12 *high-level radioactive waste (HLRW or HLW)*—(*a*) the highly radioactive material resulting from the reprocessing of spent nuclear fuel, including liquid waste produced directly in reprocessing and any solid material derived from such liquid waste that contains fission products (U.S. Code Title 42, Section 10101); (*b*) liquid wastes resulting from the operation of the first cycle solvent extraction system, or equivalent, and the concentrated wastes from subsequent extraction cycles, or equivalent, in a facility for reprocessing irradiated reactor fuel.

3.1.13 *homogeneous glass*—(*1*) an inorganic product of fusion that has cooled to a rigid condition without crystallizing (see Terminology C 162); (*2*) a noncrystalline solid or an amorphous solid.[9]

3.1.14 *incidental waste*—wastes that are not classified as HLW. NRC has defined three criteria that must be met for a waste to be called incidental waste: (*1*) wastes that have been processed (or will be further processed) to remove key radionuclides to the maximum extent that is technically and economically practical; (*2*) wastes that will be incorporated in a solid physical form at a concentration that does not exceed the applicable concentrations for Class C low-level waste; and (*3*)

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[5] *Annual Book of ASTM Standards*, Vol 12.01.

[6] *Annual Book of ASTM Standards*, Vol 11.01.

[7] Perkins, W. W., (Ed.), *Ceramic Glossary*, The American Ceramic Society, 1984.

[8] *Code of Federal Regulations Title 40*, Volume 19, Part 268.

[9] Varshneya, A. K., "Fundamentals of Inorganic Glasses," Academic Press, Boston, MA, 1994.

wastes that are to be managed pursuant of the Atomic Energy Act, so that safety requirements comparable to the performance objectives set out in 10 CFR Part 61, Subpart C are satisfied.

3.1.15 *infrared incinerator*—any enclosed device that uses electric powered resistance heaters as a source of radiant heat followed by an afterburner using controlled flame combustion and which is not listed as an industrial furnace **EPA 40 CFR 260.10**

3.1.16 *incineration*—(*1*) controlled flame combustion and neither meets the criteria for classification as a boiler, sludge dryer, or carbon regeneration unit, nor is listed as an industrial furnace; or (*2*) meets the definition of infrared incinerator or plasma arc incinerator **EPA 40 CFR 260.10**

3.1.17 *Joule heating*—heating of glass by passing an electric current through it, the powerful stirring effect of the convection currents created by electric heating causes uniformity of temperature throughout the body of glass and makes it physically homogeneous.[10]

3.1.18 *loss-on-heating (LOH)*—the percent loss in weight of a material at a constant temperature ≥105°C , and for a time long enough, to achieve constant weight, expressed as a percent of the initial weight of the dry material; The fractional or percentage weight loss of a material on heating in air from an initial defined state (usually, dried) to a specified temperature, such as 1000°C, and holding there for a specified period, such as 1 hour. Fixed procedures are designed, usually, such that LOH represents the loss of combined H_2O, CO_2, certain other volatile inorganics, and combustible organic matter.[7]

3.1.19 *low-activity waste*—the low-activity portion of HLLW that is separated from the HLLW so that it can be classified as LLW and be disposed of as "incidental waste."

3.1.20 *low-level radioactive waste (LLRW or LLW)*—(*a*) LLRW is waste that satisfies the definition of LLRW in the Radioactive Waste Policy Amendments Act of 1985; radioactive material that is not high-level radioactive waste, spent nuclear fuel, or byproduct material as given in the Atomic Energy Act of 1954; (*b*) Low level wastes are also not transuranic wastes as given in the Low Level Radioactive Waste policy Amendments Act and 10 CFR Part 61; (*c*) waste that (*1*) is not high-level radioactive waste, spent nuclear fuel, or byproduct material (as defined in section IIe(2) of the Atomic Energy Act of 1954, (42 U.S.C. 2014(e)(2))); and waste that (*2*) the NRC, consistent with existing law and in accordance with paragraph (a), classifies as low-level radioactive waste. Low-level radioactive waste (LLW) is a general term for a wide range of wastes. Industries, hospitals and medical, educational, or research institutions; private or government laboratories; and nuclear fuel cycle facilities (for example, nuclear power reactors and fuel fabrication plants) using radioactive materials generate low-level wastes as part of their normal operations. These wastes are generated in many physical and chemical forms and levels of contamination **10 CFR Part 61**

3.1.21 *mixed waste*—waste that contains both hazardous waste and source special nuclear or byproduct material subject to the Atomic Energy Act (AEA) of 1954;[11] The "radioactive component" refers only to the actual radionuclides dispersed or suspended in the waste substance.[12]

3.1.22 *mixed waste glass*—a glass comprised of glass forming additives and hazardous waste that contains radioactive constituents.

3.1.23 *natural accelerator produced radioactive materials (NARM)*—radioactive materials not covered under the Atomic Energy Act of 1954 that are naturally occurring or produced by an accelerator. Accelerators are used in sub-atomic particle physics research. These materials have been traditionally regulated by States. NARM waste with more than 2 nCi/g of ^{226}Ra or equivalent is commonly referred to as discrete NARM waste; below this threshold, the waste is referred to as diffuse NARM waste. NARM waste is not covered under the Atomic Energy Act, it is not a form of LLW, and it is not regulated by Nuclear Regulatory Commission.

3.1.24 *naturally occurring radioactive materials (NORM)*—NORM refers to materials not covered under the Atomic Energy Act whose radioactivity has been enhanced (radionuclide concentrations are either increased or redistributed where they are more likely to cause exposure to man) usually by mineral extraction or processing activities. Examples are exploration and production wastes from the oil and natural gas industry and phosphate slag piles from the phosphate mining industry. This term is not used to describe or discuss the natural radioactivity of rocks and soils, or background radiation, but instead refers to materials whose radioactivity is technologically enhanced by controllable practices. Note this definition is sometimes called technically enhanced NORM or TENORM.

3.1.25 *plasma arc incinerator*—any enclosed device using a high intensity electrical discharge or arc as a source of heat followed by an afterburner using controlled flame combustion and which is not listed as an industrial furnace. **EPA 40 CFR 260.10**

3.1.26 *radioactive*—of or exhibiting radioactivity;[13] a material giving or capable of giving off, radiant energy in the form of particles or rays, as alpha, beta, and gamma rays, by the disintegration of atomic nuclei; said of certain elements, such as radium, thorium, and uranium, and their products.[14]

3.1.27 *radioactivity*—spontaneous nuclear disintegration with emission of corpuscular or electromagnetic radiation, or both. **D 1129**

3.1.28 *radioactive waste*—solid, liquid, and gaseous materials from nuclear operations that are radioactive or become radioactive and for which there is no further use. Wastes are generally classified as high-level (having radioactivity concentrations of thousands of curies per gallon or cubic foot), low-level (on the order of 1 microcurie per gallon or cubic foot), or intermediate level (between these extremes). **10 CFR Parts 60 and 61**

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[10] Meigh, E., "Electric Melting in the Glass Industry," Chapter 7, A.G. Pincus and G.M. Kiken, Books for Industry, New York, NY, 1976.

[11] *Federal Facilities Compliance Act*, 1992, (RCRA Section 1004 (41,42,USC 6903)41)).

[12] *DOE Order 5400.3*.

[13] *The American Heritage Dictionary*, Houghton Mifflin, 2nd Edition, The World Publishing Co., New York, 1973.

[14] *Webster's New Twentieth Century Dictionary*, 1973.

3.1.29 *residual radioactive material*—(*1*) waste(which the secretary of energy determines to be radioactive) in the form of tailings resulting from the processing of ores for the extraction of uranium and other valuable constituents of the ore; and (*2*) other waste (which the secretary of energy determines to be radioactive) at the processing site which relates to such processing, including any residual stock of unprocessed ores or low grade-materials. This term is used only with respect to materials at sites subject to remediation under Title I of the Uranium Mill Tailings Radiation Control Act of 1978, as amended. **10 CFR Part 40**

3.1.30 *RCRA hazardous waste*—a solid waste that exhibits a characteristic of a hazardous waste or is, or contains a listed hazardous waste. A RCRA solid waste may be a solid, liquid, or gas. **40 CFR Part 261.3**

3.1.31 *RCRA listed waste*—a solid waste that has been listed by EPA by virtue of its toxicity characteristics or because of the industrial process from which it is derived. **40 CFR Part 261.11**

3.1.32 *simulated waste glass*—a glass comprised of glass forming additives with simulants of, and/or actual chemical species in radioactive wastes, mixed wastes, or heavy metal wastes.

3.1.33 *slag*—glass that contains crystalline material including metal inclusions upon exiting a thermal treatment unit (see also *glass-ceramic*).

3.1.34 *sludge*—any solid, semi-solid, or liquid waste generated from a municipal, commercial, or industrial waste water treatment plant, water supply treatment plant, or air pollution control facility exclusive of the treated effluent from a wastewater treatment plant. **40 CFR 260.10**

3.1.35 *speciation*—a calculation of the chemical species (for example, oxides, hydroxides carbonates, sulfates in wt%) present in a waste based upon the elemental analyses of a waste (in wt%) in order to predict the fractionation of each species into the final wasteform or into the off-gas.

3.1.36 *treatability study*—a study in which a hazardous waste is subjected to a treatment process to determine (*1*) whether the waste is amenable to the treatment process, (*2*) what pretreatment is required, (*3*) optimal process conditions, (*4*) efficiency of a treatment process, and (*5*) characteristics and volumes of residuals. **40 CFR 260.10**

3.1.37 *TRU waste*—waste containing more than 100 nanocuries of alpha-emitting transuranic isotopes, with half-lives greater than twenty years, per gram of waste, except for (*1*) high-level radioactive waste; (*2*) wastes that DOE has determined, with the concurrence of EPA, do not need the degree of isolation required by EPA's high level waste rule (40 CFR 191); or (*3*) has approved for disposal on a case-by-case basis in accordance with NRC's radioactive land disposal regulation (10 CFR Part 61). TRU is not generally found outside the DOE complex and is mainly produced from the reprocessing of spent nuclear fuel, nuclear weapons production, and reactor fuel assembly. TRU wastes mainly emit alpha particles as they break-down. DOE categorizes TRU as either Contact Handled (CH) or Remote Handled (RH) with RH being the more radioactive of the two.

3.1.38 *uranium milling*—any activity that results in the production of byproduct material.

3.1.39 *uranium mill tailings*—see *byproduct material* and/or *residual radioactive material*.

3.1.40 *vitrification*—the process of fusing waste or simulated waste with glass making chemicals at elevated temperatures to form a waste glass or a simulated waste glass. **C 162**

3.1.41 *waste*—any residue containing radioactive or hazardous materials not currently considered useful or economically recoverable. **C 859**

3.1.42 *waste characterization*—sampling, monitoring, and analysis activities to determine the extent and nature of a waste.

3.1.43 *waste form*—the waste materials and any encapsulating or stabilizing matrix/materials.

3.1.44 *weight percent solids*—the percent weight remaining after a material has been dried (see also *drying*) at 105°C, for a time long enough, to achieve constant weight, expressed as a percent of the initial weight of the material, for example, the initial weight of the material minus the amount of water or other volatiles lost upon drying at 105°C.

4. Significance and Use

4.1 This guide identifies methods to determine the physical and chemical characteristics of a variety of hazardous and/or radioactive wastes including heavy metal contaminated wastes. These wastes can be in the physical form of sludges (wet or dry), spent waste water filter aids, waste water filter cakes, incinerator ashes (wet or dry), incinerator blowdown (wet or dry), asbestos, resins, zeolites, soils, unset or unsatisfactory cementitious waste forms in need of remediation, lead paint wastes, radioactively or non-radioactively contaminated asbestos, geologic mill tailings (also known as byproduct materials) and other naturally occurring or accelerator produced radioactive materials (NORM and NARM), etc. and combinations of the above. This guide may not be applicable to piping, duct work, rubble, debris waste or wastes containing these components.

4.1.1 This guide identifies the physical and chemical characteristics useful for developing high temperature thermal treatment methodologies for a variety of hazardous and/or radioactive process wastes and soils including heavy metal contaminated wastes. The waste characteristics can be used to (*1*) choose and develop the thermal treatment methodology, (*2*) determine if waste pretreatment is needed, (*3*) aid in development of thermal treatment process control, (*4*) develop surrogate waste formulations, (*5*) perform treatability studies, (*6*) determine processing regions (envelopes) of acceptable waste form composition, and/or (*7*) perform pilot scale testing with actual or surrogate waste, and/or (*8*) determine the composition and concentrations of off-gas species for regulatory compliance.

4.2 This guide identifies applicable test methods that can be used to measure the desired characteristics of the hazardous and/or radioactive wastes described in 4.1. The analyses discussed in this standard can be performed by a variety of techniques depending on equipment availability. For example, Gas Chromatograph Mass Spectrometry (GC/MS) can be used to measure the amount and type of off-gas species present. However, this standard assumes that such sophisticated equipment is unavailable for radioactive or hazardous waste service due to potential contamination of the equipment. The analyses recommended are, therefore, the simplest and least costly analyses that can be performed and still considered adequate. Not every characteristic given in this guide is necessary for every waste (see Fig. 1). Cation analysis is necessary for every waste in order to determine whether the final waste form will be a homogeneous glass, a glass-ceramic, or a slag (see Appendix X1).

4.2.1 Waste Analysis Method A is applicable when it is desired to know the amount and type of volatiles to be expected during thermal treatment and their compatibility with the thermal treatment and off-gas unit materials of construction and design capacity. These methods may be used to determine incinerator off-gas composition and concentrations.

4.2.2 Waste analysis Method A is applicable when it is necessary to know the amount of organics in the waste independently of the amount of other volatile constituents present for safety concerns. These methods may be used to determine incinerator off-gas composition and concentrations.

4.2.3 Waste analysis Method A is applicable when it is necessary to know if molten salt formation and accumulation in a thermal treatment unit in the presence of water vapor may be a safety concern.

4.2.4 Waste Analysis Methods B and C are applicable when it is desired to only know the amount of volatiles to be expected during thermal treatment, for example, when speciation of the volatiles and potential molten salt formation is not of concern. These methods may be used to determine the total concentration of incinerator off-gases.

4.3 Data from these tests may form part of the larger body of data that are necessary in the logical approach to development of high temperature treatment and/or pretreatment methodologies for a variety of hazardous and/or radioactive wastes as described in 4.1.

5. Summary of Waste Characteristics

5.1 Table 1 lists the waste characteristics that should be considered before a waste is processed in a high temperature thermal treatment apparatus. Table 1 describes the rationale for considering each characteristic.

5.2 Test Method A provides analysis of the weight percent solids, identification of the constituents and their concentrations that will vaporize during thermal treatment, identification of problematic anions that can attack materials of construction and/or form hazardous molten salt layers, and identification of the waste constituents and their concentrations that will be incorporated into the final glass, glass-ceramic, or slag.

5.3 Test Methods B and C can be used to determine total wt% LOH but not the LOH speciation. Test Methods B and C will also not provide organic analyses, anion analyses, and reduction/oxidation analyses.

6. Test Method A

NOTE 2—Note Method C should be used rather than Method B when the waste is very refractory.

6.1 Waste analysis Method A uses wastes that have been dried at 105 ± 2°C. The waste analysis strategy for Method A is given in Fig. 2. Method A provides analysis of the weight percent solids, identification of the constituents and their concentrations that will vaporize during thermal treatment, identification of problematic anions that can attack materials of construction and/or form hazardous molten salt layers, and identification of the waste constituents and their concentrations that will be incorporated into the final glass, glass-ceramic, or slag.

6.2 *Weight Percent Solids/Loss-on-Heating*—Weigh empty crucible. Weigh waste plus crucible before drying. Dry waste in crucible at 105°C until a constant weight is achieved to determine the weight percent (wt%) solids and Loss-On-Heating (wt% LOH) of water, if any, at this temperature. X-ray diffraction (XRD) analysis of the dried waste determines what phases are present. If hydroxide and/or carbonate species are identified in XRD analysis, additional Loss-on-Heating analyses at 300°C and 1000°C will be necessary (see 6.8 and 6.9). Calculate the wt% solids and wt% LOH at 105°C by the following:

$$\text{wt\% solids} = \{(W_3 - W_1)_{105^\circ\text{C}} / (W_2 - W_1)_{\text{rt}}\} \cdot 100 \tag{1}$$

$$(\text{wt\% LOH})_{105^\circ\text{C}} = \{(W_2 - W_1)_{\text{rt}} - (W_3 - W_1)_{105^\circ\text{C}}\} / \{(W_2 - W_1)_{\text{rt}}\} \cdot 100$$

$$\text{wt\% solids} + (\text{wt\% LOH})_{105^\circ\text{C}} = 100\ \%$$

where:

W_1 = weight of the crucible,
W_2 = weight of crucible and waste prior to drying, and
W_3 = weight of crucible and waste after drying at 105°C.

6.2.1 The weight % solids and the wt% $(\text{LOH})_{105^\circ\text{C}}$ should sum to 100 %.

6.3 *Cation Analyses*—Dissolution using fuming perchloric acid as used in the commercial glass industry (see Methods C 169) is not recommended for radioactive samples as the fumes can cause radioactive species to become airborne and present inhalation and radionuclide uptake hazards to the user. Alternative dissolution methodologies are given in 6.3.1-6.3.5.

6.3.1 *HF/HN0$_3$ Microwave Dissolution (ASTM C 1463)*—This methodology may be used to dissolve waste(s) but the user is cautioned that this dissolution methodology must be coupled with other dissolution methologies in order for a complete analysis to be achieved. The HF in this dissolution methodology compromises analysis of elements such as Si which form SiF_4 colloids which precipitate from the dissolution extract before Inductively Coupled Plasma Atomic Emission Spectroscopy (ICP-AES), Atomic Absorption (AA) Spectroscopy, Atomic Emission (AE) spectroscopy, and/or ICP Mass Spectroscopy (ICP-MS) analysis can be completed.

6.3.2 *Na_2O_2 or KOH Fusion/HCl Dissolution (ASTM C 1317 and C 1463)*—This dissolution methodology may be used to dissolve waste(s) but the user is cautioned that these methods cannot be used for analysis of Na^+, K^+ and other alkalis that may be major components or impurities in the starting Na_2O_2 or KOH. The sample is fused with Na_2O_2 or KOH at elevated temperature and the fused residue dissolved in water and then acidified with HCl. Dissolutions with HCl

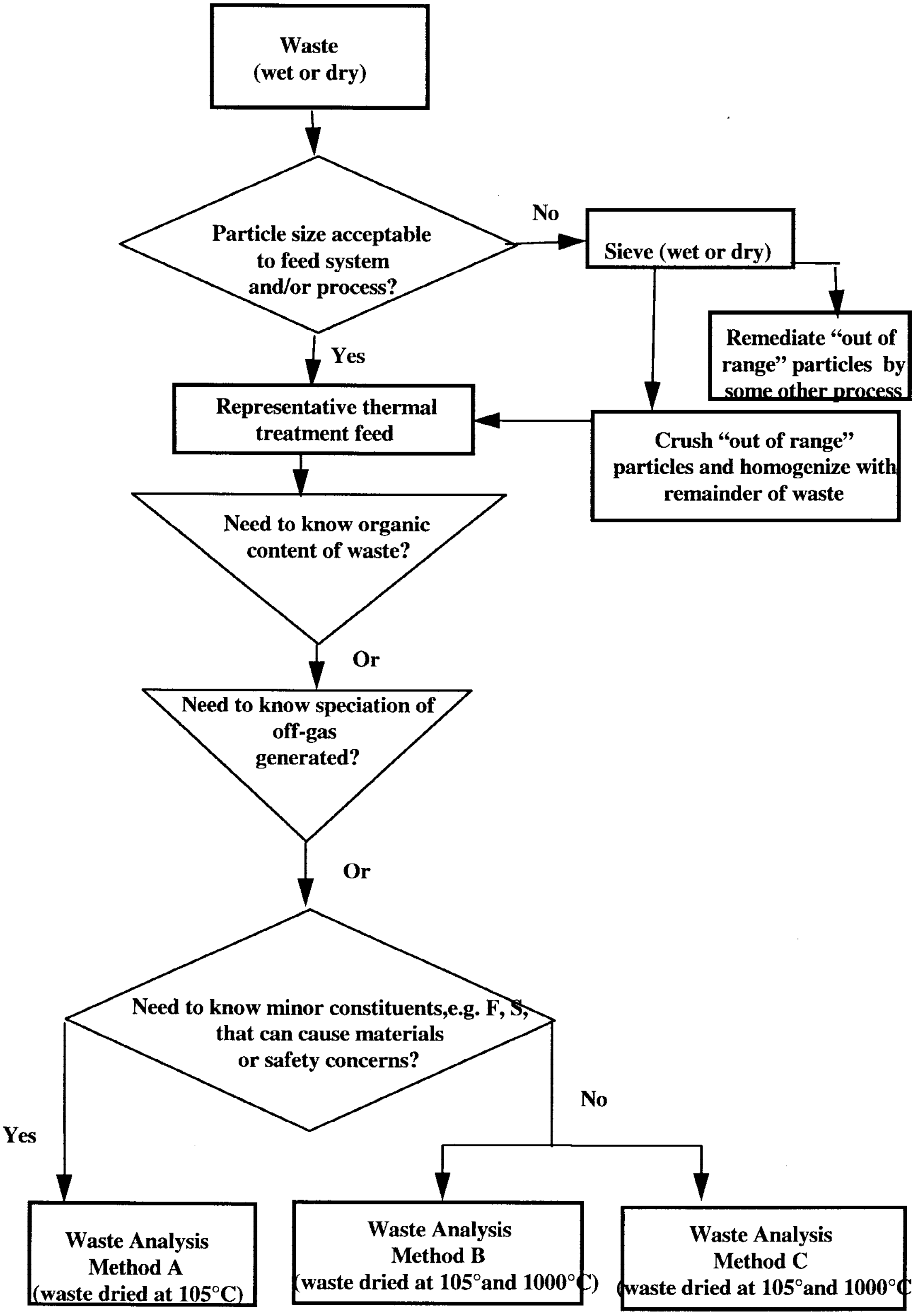

FIG. 1 Choice of Test Methods

uptake give excellent reproducible extracts that can be ana-

TABLE 1 Waste Characteristics to be Considered Prior to High Temperature Thermal Treatment

Waste Attribute	Rationale
Particle Size	Determination of adequacy of feed system, mixing system, and homogeneity of final waste form, for example, large (≥ 2.5 cm) dense particles like pebbles may not vitrify. See Test Methods C 92
Homogeneity	Determination of number of replicate waste analyses that need to be performed; to design process control system to handle waste variability; determination of whether additional process vessels for homogenization of waste are necessary
Total Loss-On- Heating (LOH) at Treatment Temperature in wt%	Sizing of off-gas system to handle total volume of volatiles, for example, steam (H_2O, OH^-), CO_2, SO_x, NO_x, that are generated during thermal processing, for example, can range from 1 to 98 % or evaluation of potential waste loading.
LOH speciation	Adequacy of off-gas system components and materials of construction to handle the types of off-gas anticipated, for example, acid gasses (NO_x as HNO_3 vapor, SO_x as H_2SO_4 vapor), F, Cl, etc.; design adequate filtration.
Total Radioactivity	Hazards analysis, for example, shielding and safety concerns; design of adequate filtration to achieve desired decontamination factors (DF's) before off-gas is quenched and/or released to the atmosphere.
Radionuclide or Hazardous Constituent Speciation	Choice of thermal treatment temperature, for example, radionuclides as Cs-137 and Tc-99 are volatile at ≥1150°C , to ensure that radionuclides are retained in the vitrified waste form
Volatile Constituent Speciation	Choice of thermal treatment temperature for minimization or elimination of volatilization (secondary waste generation) of hazardous components such as Se , As, Tc-99, Cs-137. Determination of whether SO_x will be liberated as SO_3, SO_2 or S_2 depending on treatment temperature and oxidation state of the waste, for example, at 1150°C ~50 % $SO_4^=$ is volatilized while at ~1500°C about 90 % is volatilized.
Organics (TC = Total Carbon and TOC = Total Organic Carbon) in wt%	Safety concerns, >5 wt% organics can cause safety concerns in certain types of thermal treatment units; design pretreatment methods to limit organics to <5 wt%.
Anions (in wt%)	wt% LOH speciation, for example, SO_x, NO_x, F, and Cl specifically; needed to know potential for molten salt (for example, (K,Na,Cs)Cl, (K, Na,Cs)F, $(K,Na, Cs)_2SO_4$) as a secondary phase in the vitrified waste form, for example, molten salt layers can cause steam explosions in certain types of thermal treatment units; needed to know for potential attack on materials of construction of thermal treatment unit, for example, electrodes and refractories; needed to know if velocity in off-gas line is adequate to prevent pluggage from molten salt accumulations.[A]
Cations (in wt%)	Determination of glass forming or slagging system of choice (see Appendix X1); to maximize waste loading; choice of glass additives; potential attack on materials of construction of thermal treatment unit, for example, electrodes and refractories
Reduction/Oxidation (REDOX) Potential	Choice of pretreatment; addition of oxidizers as glass formers to prevent formation of metallic and/or sulfide phases which can cause certain thermal treatment units with metallic electrodes to short and/or attack materials of construction; design of pretreatment.

[A] Jantzen, C. M., Choi, A.S., Randall, C. T., "Glass Melter Off-gas System Pluggages: Cause, Significance, and Remediation," *Proceedings of the 5th International Symposium on Ceramics in Nuclear Waste Management*, G. G. Wicks, D. F. Bickford, and R. Bunnell (Eds.), American Ceramic Society, Westerville, OH, 621-630 (1991); Jantzen, C. M., "Characterization of Off-Gas System Pluggages, Significance for DWPF and Suggested Remediation," *U.S. DOE Report WSRC-TR-90-205*, 1991, p. 72; Jantzen, C. M., Choi, A. S., and Randall, C. T., "Remediation of Off-Gas System Deposits in a Radioactive Waste Glass Melter," *High Level Radioactive Waste and Spent Fuel Management*, Vol 2, S. C. Slate, L. C. Oyen, K. J. Lee, and W. Z. Oh (Eds.), Korean Nuclear Society, Seoul, Korea, 1991, pp. 21-32.

lyzed by Inductively Coupled Plasma Atomic Emission Spectroscopy (ICP-AES), Atomic Absorption (AA) Spectroscopy, and/or ICP Mass Spectroscopy (ICP-MS) for most elements including Si, Al, B, and radionuclides.

6.3.3 *Aqua Regia Dissolution*[15]— This dissolution methodology may be used to dissolve waste(s) and is extremely aggressive to minor hazardous and heavy metal constituents. The analytic extract can be analyzed by Inductively Coupled Plasma Atomic Emission Spectroscopy (ICP-AES), Atomic Absorption (AA)Spectroscopy, and/or ICP Mass Spectroscopy (ICP-MS).

6.3.4 *Alkali Metaborate Dissolution (ASTM C 1463)*[16]— This dissolution methodology may be used to dissolve waste(s) and is extremely aggressive. The sample is fused with $LiBO_2$ or $NaBO_2$ at elevated temperature (900°C) for 15 min in a platinum crucible. The user is cautioned that this method

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[15] Coleman, C. J., "Aqua Regia Dissolution of Sludge for Elemental Analysis," *WSRC-RP-90-371*, 1990.

[16] Crow, R. F., and Connolly, J. D., "Atomic Absorption Analysis of Portland Cement and Raw Mix Using Lithium Metaborate Fusion," *Jour. Test. Evaluation*, 1, 1973, pp. 382-393.

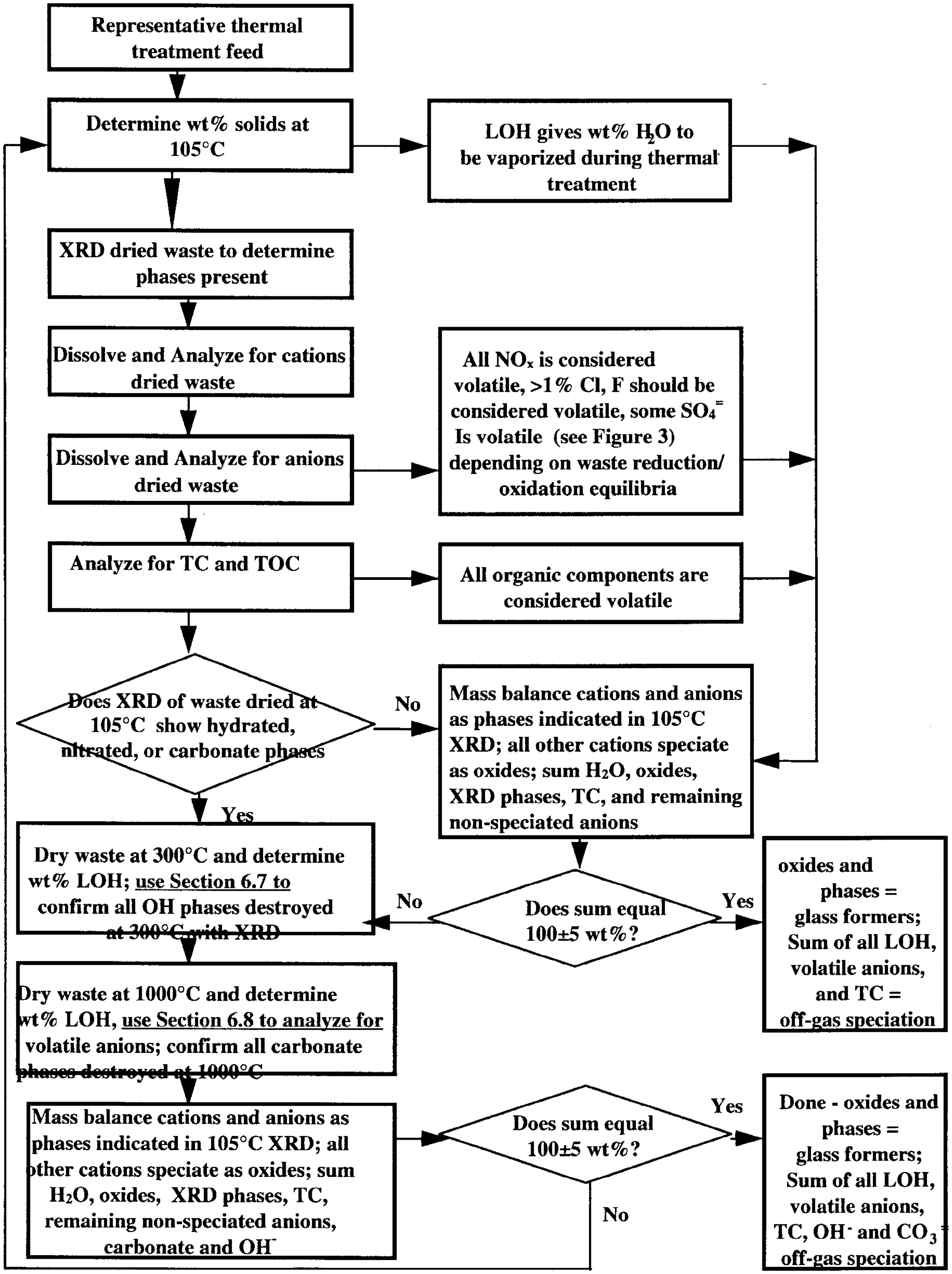

FIG. 2 Waste Analysis Method A

prohibits analysis of B^{+3} and Na^{+} or Li^{+} depending on which alkali metaborate is chosen as a fusion flux. However, if waste is known not to contain Li^{+} or B^{+3} this method can be used for all other cations and radionuclides. The bottom of the crucible is quenched in water and the fused material is dissolved in 4 % HNO_3 and diluted as necessary. The analytic extract can be analyzed by Inductively Coupled Plasma Atomic Emission Spectroscopy (ICP-AES), Atomic Absorption (AA)Spectroscopy, and/or ICP Mass Spectroscopy (ICP-MS).

6.3.5 *EPA SW-846 Method 3050 Dissolution*—This methodology may be used to dissolve waste(s) for analysis but the user is cautioned that this dissolution is primarily an extract of elements which are soluble in nitric acid from the waste matrix. This methodology, and other wet digestions that either do not incorporate HF, or do not fuse the sludge or soil in a flux before dissolution, may not lead to dissolution of the metals incorporated into aluminosilicate matrices (for example, soils, sediment, ashes, sludges, asbestos, etc.) and thus may underestimate constituents of potential interest (for example, Si) to the application of a given treatment technology.[17,18] The leachate can be analyzed by Inductively Coupled Plasma Atomic Emission Spectroscopy (ICP-AES), Atomic Absorption (AA) Spectroscopy, and/or ICP Mass Spectroscopy (ICP-MS).

6.4 *Anion Analysis*:

6.4.1 *Na_2O_2 Fusion/H_2O Dissolution (ASTM C 1317)*—A sample of waste is fused with Na_2O_2 or KOH at elevated temperature and the fused residue dissolved in water. The residue is NOT dissolved in HCl per Practice C 1317. Dissolutions with H_2O provide analytic extracts which can be analyzed by Ion Chromotography (IC) see Test Method D 4237 or Ion Selective Electrode (ISE) for wt% anions of concern.

6.5 *Radiochemical Analysis*—or radionuclides which are not dissolved by the above methodologies, and cannot be measured by ICP-AES or ICP-MS consult "DOE Methods for Evaluating Environmental and Waste Management Samples" (March, 1993, DOE.EM-0089T, Rev. 1), and/or EPA SW846, and/or Radioanalytical Technology for 10 CFR Part 61 and Other Selected Radionuclides, Literature Review, C. W. Thomas, V. W. Thomas, and D. E. Robertson, PNNL-9444 (March, 1996), and/or Practice C 1168.

6.6 *Carbon Analysis*—Typically knowledge of the amounts of Total Carbon (TC) and Total Inorganic Carbon (TIC) is sufficient for determination of the appropriate thermal treatment option. Total Organic Carbon (TOC) is determined as the difference between TC and TIC (refer to EPA SW846). If detailed speciation of organics is deemed necessary consult "DOE Methods for Evaluating Environmental and Waste Management Samples" (March, 1993, DOE.EM-0089T, Rev. 1), and/or EPA SW846.

6.7 Fe^{+2}/Fe^{+3} *or* $Fe^{+2}/\Sigma Fe$ *Analysis*—For wastes containing large concentrations of iron the colorimentric analysis by Baumann[19] or Goldman,[20] or Mossbauer Spectroscopy are the preferred methodologies. In the Baumann methodology, shown to be the simplist to perform remotely on highly radioactive wastes,[19] the waste dried at 105°C is dissolved by H_2SO_4/HF in the presence of NH_4VO_3 and the amount of Fe^{+2} is measured colorimetrically. All of the iron is reduced to the Fe^{+2} state by ascorbic acid and the total iron (ΣFe) measured. From these two measurements either the Fe^{+2}/Fe^{+3} or $Fe^{+2}/\Sigma Fe$ ratios can be calculated. Alternatively, Test Methods C 146 can be used when the iron concentrations are expected to be less than ~1 wt% (Test Methods C 146). The iron redox ratios serve as an indicator of the oxidation/reduction equilibria expected in the thermal treatment unit and in the final vitrified product. Known[21] electro-motive-forces (EMF) can be used to determine the oxidation state of other species, S versus $SO_4^{=}$ once the indicator iron redox ratios are known.

6.8 *Calculation of OH^- Content of the Waste*—Weigh empty crucible. Weigh waste plus crucible before drying. Dry waste at ~300°C until a constant weight is achieved to determine the Loss-on-Heating at 300°C. Perform phase analysis by x-ray diffraction on the dried sample. Examine the XRD pattern to determine if the hydroxide phases identified in 6.2 have been destroyed by the 300°C heat treatment. Calculate the wt% LOH at 300°C by the following:

$$(\text{wt\% LOH})_{300°C} = \{\{(W_2 - W_1)_{rt} - (W_3 - W_1)_{300°C}\} / (W_2 - W_1)_{rt}\} \cdot 100 \quad (2)$$

where:

W_1 = weight of the crucible,
W_2 = weight of crucible and waste prior to heating, and
W_3 = weight of crucible and waste after drying at 300°C.

6.8.1 The difference between the $(\text{wt\% LOH})_{105°C}$ and the $(\text{wt\% LOH})_{300°C}$ is a good approximation of the sum of the weight percent of structurally bound OH^- in the waste species, for example, $Al(OH)_3$, $Fe(OH)_3$, etc. and the Total Organic Carbon (TOC).

6.8.2 Calculate the OH^- contribution of the waste by the following:

$$OH^-(\text{wt\%}) \approx (\text{wt\% LOH})_{300°C} - (\text{wt\% LOH})_{105°C} - \text{TOC} \quad (3)$$

6.9 *Calculation of $CO_3^{=}$ Content (wt%) of the Waste*—Ideally, the amount of $CO_3^{=}$ can be measured by Gas Chromatography and Mass Spectrometry (GC/MS). However, for applications where a GC/MS is not available and/or the waste is highly variable, the following estimations on a larger bulk sample are sufficient to determine if a waste is a candidate for thermal treatment, the approximate volume reduction that will be achieved, and the needed capacity for the off-gas treatment.

6.9.1 Weigh empty crucible. Weigh waste plus crucible before drying. Dry waste at ~1000°C until a constant weight is achieved to determine the Loss-on-Heating at 1000°C. Perform phase analysis by x-ray diffraction on the dried sample. Examine the XRD pattern to determine if any carbonate phases identified in 6.2 have been destroyed by the 1000°C heat treatment.

6.9.2 Calculate the wt% LOH at 1000°C by the following:

$$(\text{wt\% LOH})_{1000°C} = \quad (4)$$

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[17] Gao, D., and Silox, G. D., "The Effect of Treatment Temperature on Metal Recovery from a Porous Silica Sorbent by EPA Method 3050 and by an HF-Based Methodology," *Air & Waste*, 43, 1993, p. 1004.

[18] Bostick, W. D., Hoffmann, D. P., Stevenson, R. J., Richmond, A. A., and Bickford, D. F., "Surrogate Formulations for Thermal Treatment of Low-Level Mixed Waste, Part IV: Wastewater Treatment Sludges," *U.S. DOE Report DOE/MWIP-18*, Martin Marietta Energy Systems, Inc., January, 1994.

[19] E. W. Baumann, "Colorimetric Determination of Iron (II) and Iron (III) in Glass," *Analyst*, Vol 117, 1992, pp. 913-916.

[20] Goldman, D. S., "Investigation of Potential Analytical Methods for Redox Control of the Vitrification Process," *USDOE Report PNL-5581*, Battelle-Pacific Northwest Laboratory, Richland, WA, November 1985.

[21] Schreiber, H. D., and Hockman, A. L., "Redox Chemistry in Candidate Glasses for Nuclear Waste Immobilization," *J. Am. Ceram. Soc.*, 70[8], 1987, pp. 591-594.

$$\{(W_2 - W_1)_{rt} - (W_3 - W_1)_{1000°C}\} / \{(W_2 - W_1)_{rt}\} \cdot 100$$

where:

W_1 = weight of the crucible,
W_2 = weight of crucible and waste at room temperature (rt), and
W_3 = weight of crucible and waste after drying at 1000°C.

6.9.3 The difference between the (wt% LOH)$_{300°C}$ and the (wt% LOH)$_{1000°C}$ is a good approximation of the weight percent $CO_3^=$ in the waste species, for example, $CaCO_3$, and the nitrate (wt% NO_3^-) and nitrite (wt% NO_2^-) content. Since the nitrate (wt% NO_3) and nitrite (wt% NO_2^-) content have been measured in 6.4, the $CO_3^=$ wt% contribution of the waste can be calculated by the following:

$$CO_3^=(wt\%) \approx \qquad (5)$$

$$(wt\%\ LOH)_{1000°C} - (wt\%\ LOH)_{300°C} - (wt\%\ NO_2^-) - (wt\%\ NO_3^-)$$

6.9.4 $CO_3^=$ wt% can also be obtained from the Total Inorganic Carbon (wt% TIC) as defined in 6.6.

6.10 *Complete Waste Analysis After Drying at 105°C*—In order to obtain a complete waste analysis, waste should be dried at 105°C and dissolved by more than one of the methods given in 6.3 and 6.4: no one dissolution methodology gives all of the major cations of concern. Combinations of the dissolution methodologies and analytic methodologies given above need to be employed as in the following example:

6.10.1 Dissolution by $LiBO_2$ fusion with an HNO_3 uptake:

6.10.1.1 ICP (see Test Methods C 1109 and/or Test Method C 1111)—Typically cations such as Al, Ca, Fe, Mg, Mn, Si, Cr, Ni, Na, Zr, Sr, Ti, P, Ba, Pb, Mo, Zn, Cu, U are obtained. See 6.5 for radiochemical analyses of concern.

6.10.1.2 AA—Typically cations such as Ni, Na, K, Si are obtained. Note that this is one of the few methods available for the determination of potassium (K).

6.10.2 Dissolution by Na_2O_2 fusion with an HCl uptake:

6.10.2.1 ICP (see Test Methods C 1109 and/or Test Method C 1111)—Typically cations such as Al, B, Ca, Fe, Mg, Mn, Si, Cr, Li, Sr, Ti, P, Ba, Pb, Mo, Zn, Cu, U are obtained. Na cannot be determined with this method. If a zirconia crucible is used for the fusion, then Zr cannot be determined by this method. If a nickel crucible is used for the fusion, then Ni cannot be determined by this method. See 6.5 for radiochemical analyses of concern.

6.10.3 Dissolution by Na_2O_2 with a H_2O uptake:

6.10.3.1 IC for $SO_4^=$, NO_3-, NO_2^-, $PO_4^{\approx}$

6.10.3.2 ISE for Cl^- and F^-

6.10.4 Loss-On-Heating up to ~1000°C:

6.10.4.1 $\Sigma \approx OH^- + (CO_3^=) + (NO_2^-) + (NO_3^-) + TOC$

6.11 *Analysis Accuracy by Mass Balance for Method A*:

6.11.1 *Cations*—All of the cation element weight percents determined in 6.3 should be converted to equivalent oxide concentrations in weight percent since thermally treated waste forms are primarily oxide based (Table 2). The relative

TABLE 2 Method A Analysis of a Sludge After Drying at 105°C to Remove Water and the Conversion of the Sludge Analysis to a Calcine or Oxide Forming Basis

Cations and Anions	Waste Analysis (Element Wt%)		Oxides and Anions	Major Components to be Considered for Waste Form Development (Wt%)		
	Replicate A	Replicate B		Replicate A	Replicate B	Average
Al	3.66	3.69	Al_2O_3	6.92	6.97	6.94
B	<0.01	<0.01	B_2O_3	---	---	---
Ba	<0.01	<0.01	BaO	---	---	---
Ca	5.00	5.02	CaO	7.00	7.02	7.01
Cd	0.107	0.109	CdO	0.12	0.12	0.12
Cr	<0.07	<0.07	Cr_2O_3	---	---	---
Cu	1.41	1.42	Cu_2O	0.79	0.80	0.80
	---	---	CuO	0.88	0.89	0.89
Fe	13.9	14.1	Fe_2O_3	18.78	19.05	18.92
	---	---	FeO	0.98	0.99	0.99
K	<0.15	<0.15	K_2O	---	---	---
Li	0.012	0.017	Li_2O	0.03	0.04	0.03
Mg	3.14	2.99	MgO	5.21	4.96	5.08
Mn	9.5 5	9.58	MnO	12.33	12.37	12.35
Mo	<0.01	<0.01	MoO	---	---	---
Na	0.182	0.183	Na_2O	0.25	0.25	0.25
Ni	<0.02	<0.02	NiO	---	---	---
PO_4	<0.1	<0.1	P_2O_5	---	---	---
Pb	<0.06	<0.06	PbO	---	---	---
Sb	<0.03	<0.033	Sb_2O_3	0.04	0.04	0.04
Si	4.04	3.94	SiO_2	8.64	8.43	8.54
Sr	<0.01	<0.01	SrO	---	---	---
Ti	<0.01	<0.01	TiO_2	---	---	---
Zn	20.5	20.7	ZnO	25.52	25.77	25.64
Zr	<0.02	<0.02	ZrO_2	---	---	---
$SO_4^=$	4.84	4.74	$SO_4^=$	4.84	4.74	4.79
F^-	0.342	0.322	F^-	0.342	0.322	0332
Cl^-	0.696	0.791	Cl^-	0.696	0.791	0.744
NO_2^-	<0.01	<0.01	NO_2^-	---	---	---
NO_3^-	0.486	0.505	NO_3^-	0.486	0.505	0.496
			$LOH^{A}_{>105°C}$	2.2	2.2	2.2
			SUMS	96.05	96.26	96.16

[A] wt% $LOH_{>105°C}$ = OH^- and CO_2 and TOC = 1.5 + 0.8 · (44/60) + 0 = 2.09

amounts of FeO and Fe_2O_3 shown in Table 2 are derived from the redox analyes. All of the Mn will be present as MnO if there is any FeO or Fe^{+2} component in the waste.

6.11.2 *Volatile Anions*—For the purpose of mass balance, the wt% NO_2^-, and wt% NO_3^- anionic species need not be associated with their respective cations, for example, $NaNO_3$, since the wt% $NaNO_3$ component is broken down in the mass balance calculation to wt% Na_2O in the waste form and wt% NO_3^- + wt% NO_2^- in the off-gas. Nitrates may enter the off-gas as NO_x species, N_2 or HNO_3 depending on temperature, redox, and the presence of water vapor. For the purpose of mass balance calculations, speciation as wt% NO_3^- and wt% NO_2^- is sufficient. The wt% $CO_3^=$ anionic species should be calculated as wt% CO_2 since waste species such as $CaCO_3$ is represented in the mass balance as wt% CaO in the waste form plus wt% CO_2 in the off-gas by the following relationship:

$$\text{wt\% } CO_2 \text{ gas} = CO_3^{=}(\text{wt\%}) \cdot 44/60 \tag{6}$$

where the ratio of 44/60 is the ratio of the molecular weights of $CO_2/CO_3^=$.

6.11.3 *Semi-Volatile Anions*—For the purpose of mass balance, fluoride, chloride and sulfate can be associated as the alkali species present in the waste, for example, (Na,Cs,K)F, CaF_2, (Na,Cs,K)Cl, $(Na,Cs,K)_2SO_4$ (if known), since they may be semi-volatile as NaF, NaCl, Na_2SO_4 depending on the thermal treatment temperature, the waste form composition, and the off-gas line temperature (see Table 1 and footnote A). At thermal treatment temperatures of ≤1150°C and small concentrations (≈1 wt%),[22,23] NaF, NaCl, and Na_2SO_4 may be retained in the vitrified waste form. At temperatures >1150°C, NaF and NaCl will speciate as Na_2O in the waste form and F_2, Cl_2, HF, or HCl vapors in the off-gas: F_2 and Cl_2 will form if dry waste is being processed and HF or HCl will form if water vapor is present. Sulfates such as $(Na,Cs,K)_2SO_4$ are favored if oxidized conditions exist in the thermal treatment unit. For the example given in Table 1 with high ZnO content, the sulfate species may well be $ZnSO_4$. Reducing conditions in the thermal treatment unit will favor decomposition of $SO_4^=$ anionic species to SO_3 gas and/or SO_2 gas and/or H_2SO_4 generation depending on the absence or presence of water vapor. Highly reduced conditions will favor S_2 or H_2S generation, the latter of which is highly toxic. Since the anion analyses are done on wastes dried only to 105°C, the semi-volatile anions are included in the analysis. In order to simplify the mass balance calculation, it is convenient to express the fluoride, chloride and sulfate as anions that may vaporize upon thermal treatment, for example, F^-, Cl^- and $SO_4^=$, recognizing that these anions partition to the off-gas depending on thermal treatment temperature, waste form composition, presence of water vapor, and the reduction/oxidation equilibria in the thermal treatment unit. This will be discussed in more detail in 6.13.

6.11.4 *Total Mass Balance*—The cations converted to a wt% oxide basis, plus the individual anions (F^-, Cl^-, $SO_4^=$, $NO3^-$, and NO_2^-), plus the volatile OH^- and CO_2 determined in 6.8 and 6.9, plus the TOC should sum to 100 ± 5 wt%. The summation of all of these species serves as an accurate assessment of the overall measured composition using Method A.

6.12 *Calculation of Waste Loading and Treatment Basis*:

6.12.1 *Calculation of the Calcined Oxide Basis*—The treatment basis and waste loading are defined on an oxide or calcine basis. The calcine basis is normally taken to be ~1000°C so that all the water (steam) plus volatile species (wt% OH^-, CO_2, NO_x) have been vaporized. Then the amount of the semi-volatile anions being vaporized, or alternatively, the amount of the semi-volatiles being retained in the waste form, at a particular thermal treatment temperature can be determined. In the example shown in Table 2, the wt% OH^-, CO_2, TOC, NO_2^-, and NO_3^- would completely volatilize at treatment temperatures ≤1000°C while partial volatilization of Cl^-, F^-, and $SO_4^=$ depends on the treatment temperature, the amount of the species present, the form that it is present in the waste, and the oxidation state of the melt. For example, if a treatment temperature of 1150°C is used, then Cl^- and F^- can be retained in the waste form up to a few wt% as NaF or NaCl. Under oxidizing melt conditions at the treatment temperature of 1150°C, about 37 % of the $SO_4^=$ is vaporized according to the relationship between $SO_4^=$ vaporization and thermal treatment temperature given in Fig. 3.[24] Therefore, 37 % of the $SO_4^=$ is removed from the analysis in Table 2 as well, and the entire table is renormalized to an oxide or calcine basis. If the thermal treatment conditions are reducing, for example, when large concentrations of organics are present, and/or if a thick cold cap of feed blankets the melt pool in the thermal treatment unit, then varying amounts of $SO_4^=$ can be retained other than those indicated by Fig. 3. This provides the calcine basis for determining the glass forming potential of the waste (see Appendix X1) and the waste loading (see 6.12.2).

6.12.2 The calcine oxide analysis in Table 4 can be used to determine the glass or ceramic forming potential of the waste via phase diagrams such as those given in the examples in Appendix X1. Alternatively, the glass or ceramic forming potential of a waste may be limited by certain hard to stabilize constituents that can degrade the performance of the waste form. For example, if a Joule heated melter is being slurry fed, formation of a molten salt layer composed of Na_2SO_4 that floats on the melt pool could cause steam accumulations under the salt layer and pose a safety hazard. If operating at a melt temperature of 1150°C under oxidizing conditions with a waste of the composition similar to Table 4, the amount of sulfate allowable in the waste form would be ~0.7 $SO_4^=$ (equivalent to

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[22] Bickford, D. F., Applewhite-Ramsey, A., Jantzen, C. M., and Brown, K. G., "Control of Radioactive Waste Glass Melters: I, Preliminary General Limits at Savannah River," *J. Am. Ceram. Soc*, 73 [10], 1990, pp. 2896-2902.

[23] Cozzi, A. D., Jantzen, C. M., Brown, K. G., and Cicero-Herman, C. A., "Process Control for Simultaneous Vitrification of Two Mixed Waste Streams in the Transportable Vitrification System (TVS)," *Environmental Issues and Waste Management Technologies in the Ceramic and Nuclear Industries*, Vol IV, Ceramic Transactions, v. 93, J. Marra and D. K. Peeler (Eds.), American Ceramic Society, Westerville, OH, 1999, pp. 97-105.

[24] Jantzen, C. M., Schumacher, R. F., and Pickett, J. B., "Mining Industry Waste Remediated for Recycle by Vitrification," *Environmental Issues and Waste Management Technologies VI*, D. R. Spearing, G. L. Smith, and R. L. Putnam (Eds.), American Ceramic Society, Westerville, OH, 2001, pp. 65-74.

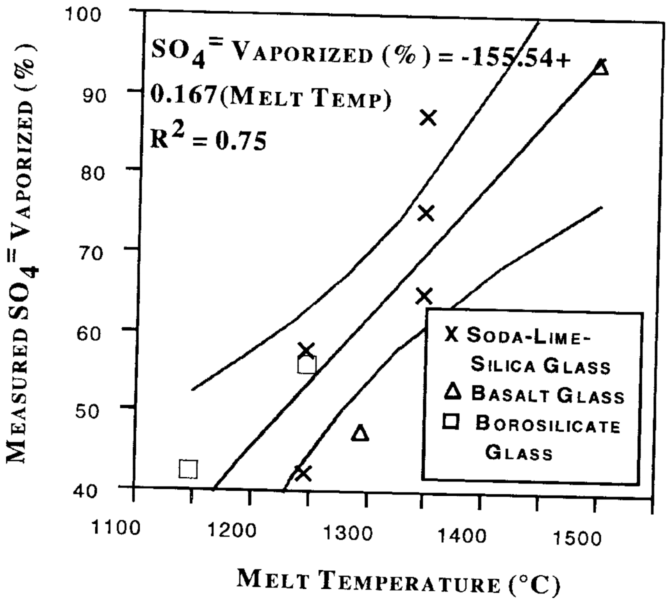


FIG. 3 Example of the Relationship of SO_4= Vaporization to Melt Temperature Under Oxidizing Conditions where wt% LOH is the Loss-on-Heating at the Anticipated Thermal Treatment Temperature

TABLE 3 Method A—Analysis of a Sludge After Drying at Various Temperatures

Drying Temperature (°C)	wt% Solids	wt% Loss-On-Ignition	Major Phases Present by X-Ray Diffraction
105	13.3	86.7	$CaCO_3$ $Al(OH)_3$ $ZnFeCrO_4$
300	11.8	88.2	$CaCO_3$ $ZnMnO_3$
1000	10.5	89.5	$ZnMnO_3$

1 wt% Na_2SO_4).[24] Therefore, waste loading could be limited to (3.29/0.7) · 100 = 21 wt% for safety considerations unless a reductant were used to enhance $SO_4^=$ vaporization, or higher temperatures were used to enhance SO_4 vaporization, or the waste contained no water to create steam.

6.12.3 Waste loading is defined as:

$$\text{Waste loading (wt\%)} = \{\text{Wt of calcine}_{(>1000)}\} / \{\text{Wt of calcine}_{(>1000°C)} + \text{Wt Glass Formers}\} \quad (7)$$

6.13 *Estimation and Identification of Off-Gases for Thermal Treatment*—Ideally, the types and volumes of off-gas species liberated from a given waste upon thermal treatment can be measured by gas chromatography and mass spectrometry (GCMS). However, for applications where a GCMS is not available and/or the waste is highly variable, estimations using the data determined in 6.2 through 6.10 are sufficient to determine if a waste is a candidate for thermal treatment, the approximate volume reduction that will be achieved, and the needed capacity for the off-gas treatment.

6.13.1 Tables 2 and 3 give an example of analytic data for a waste-water treatment sludge dried at 105°C and analyzed using the steps outlined in 6.2 through 6.10. In order to calculate the Loss-on-Heating (wt% LOH) at a given thermal treatment temperature, the wt% LOH at 105°C from Table 3 is

TABLE 4 Conversion of the Waste Analysis in Table 2 to a Calcine or Oxide Forming Basis

Oxides and Anions	Waste Analysis from Table 2 Accounting for Vaporization at the Thermal Treatment Temperature (Oxide Wt%)	Waste Analysis from Table 2 on a Calcine Basis (Oxide Wt%)
Al_2O_3	6.94	7.57
CaO	7.01	7.65
CdO	0.12	0.13
Cu_2O	0.80	0.87
CuO	0.89	0.97
Fe_2O_3	18.92	20.63
FeO	0.99	1.08
Li_2O	0.03	0.03
MgO	5.08	5.54
MnO	12.35	13.47
Na_2O	0.25	0.27
Sb_2O_3	0.04	0.04
SiO_2	8.54	9.32
ZnO	25.64	27.97
$SO_4^=$	3.02	3.29
F^-	0.74	0.81
Cl^-	0.33	0.36
SUMS	91.69	100.00

used as a starting point, for example, 86.7 wt%, and the measured wt% TOC. The wt% OH^- and CO_2 content are calculated from the wt% LOH data at 300°C and 1000°C (see 6.8 and 6.9) as follows:

$$\begin{aligned} OH^-(\text{wt\%}) &\approx (\text{wt\% LOH})_{300°C} - (\text{wt\% LOH})_{105°C} - \text{wt\% TOC} \sim 88.2 \\ &\quad - 86.7 - 0 \text{ wt\%} \\ &= 1.5\text{wt\%} \end{aligned} \quad (8)$$

$$\begin{aligned} CO_2(\text{wt\%}) &\approx \{(\text{wt\% LOH})_{1000°C} - (\text{wt\% LOH})_{300°C} - (\text{wt\% } NO_2^-) \\ &\quad - (\text{wt\% } NO_3^-)\} \cdot (44/60) \sim \{89.5 - 88.2 - 0 - 0.5\} \cdot (44/60) \\ &= 0.59\text{wt\%} \end{aligned}$$

6.13.2 The total wt% LOH between 105°C and ~1000°C is:

$$\begin{aligned} \text{wt\% LOH}_{1000-105°C} &= OH^- + CO_2 + NO_2^- + NO_3^- + TOC \\ &= 1.5 + 0.59 + 0 + 0.5 + 0 \end{aligned}$$

$$= 2.59\text{wt\%} \tag{9}$$

6.13.3 While the wt% LOH released from the wet sludge at room temperature to the off-gas (up to a temperature of ~1000°C) is:

$$\text{wt\% LOH}_{1000-25°\text{C}} = \tag{10}$$

$$H_2O(\text{steam}) + OH^- + CO_2 + NO_2^- + NO_3^- + \text{TOC} =$$

$$86.7 + 1.5 + 0.59 +0 + 0.5 + 0 = 89.3\text{wt\%}$$

6.13.4 The total wt% LOH to the off-gas system must include these species that volatilize completely (100 %) plus any contributions from Cl^-, F^-, and $SO_4^=$ which partially volatilize. The volatility of Cl^-, F^-, and $SO_4^=$ is a function of thermal treatment temperature, waste form composition, presence of water vapor, and the reduction/oxidation equilibria in the thermal treatment unit (see 6.11.3). At an 1150°C thermal treatment temperature the total wt% LOH to the off-gas per 100 lb of waste processed can be calculated as:

$$\text{wt\% LOH}_{1150°\text{C}}\,(\text{wt\%}) = \tag{11}$$

$$H_2O \text{ vapor} + OH^- + CO_2 + NO_2^- + NO_3^- + \text{TOC} +$$

$$(SO_4^= \text{ in waste times 37 \% volatilization from Fig. 3}$$

$$\text{times 21 \% waste loading dilution factor}) + F^- + Cl^- =$$

$$86.7 + 1.5 + 0.59 + 0 + 0.5 + 0 + 0.37(0.21)(4.79) + 0 + 0 =$$

$$89.7 \text{ wt\%}$$

6.13.5 At higher thermal treatment temperatures, for example, 1500°C such as those necessitated by basalt glass or basalt glass-ceramics, the Cl^- and F^- would be volatile and add another 1.07 wt% LOH to the off-gas. The $SO_4^=$ is ~95 % volatile. This leaves only 0.24 wt% $SO_4^=$ in the waste form, well below the 0.7 limit for molten salt layer formation even at 100 % waste loading. The total wt% LOH at ≈1500°C can be calculated as:

$$\text{wt\% LOH}{>}_{1500°\text{C}} = \tag{12}$$

$$H_2O \text{ vapor} + OH^- + CO_2 + NO_2^- + NO_3^- + \text{TOC} +$$

$$95\ \%\ SO_4^= + F^- + Cl^- =$$

$$86.7 + 1.5 + 0.59 + 0 + 0.5 + 0 + 0.95(4.79) + 0.33 + 0.74 =$$

$$94.9\text{wt\%}$$

7. Test Method B

7.1 Waste analysis Method B uses wastes dried at 105°C to determine the weight percent solids and wastes dried at ≥1000°C for cation analysis. The waste analyses strategy for Method B is given in Fig. 4.

7.2 *Weight Percent Solids*—Wastes should be dried at 105°C until a constant weight is achieved to determine the wt% solids at this temperature.

7.2.1 Calculate the wt% solids at 105°C by the following:

$$\text{wt\% solids} = \{(W_3 - W_1)105°\text{C} / (W_2 - W_1)_{\text{rt}}\} \cdot 100 \tag{13}$$

where:

W_1 = weight of the crucible,
W_2 = weight of crucible and waste at room temperature (rt), and
W_3 = weight of crucible and waste after drying at 105°C.

7.3 *Loss-On-Heating and Off-Gas System Loading*—Wastes should be dried at ≥1000°C until a constant weight is achieved to determine the Loss-On-Heating (wt% LOH) at this temperature. Calculate the wt% LOH at ≥1000°C by the following:

$$(\text{wt\% LOH})_{\geq 1000°\text{C}} = \tag{14}$$

$$\{(W_2 - W_1)_{\text{rt}} - (W_3 - W_1)_{\geq 1000°\text{C}} / (W_2 - W_1)_{\text{rt}}\} \cdot 100$$

where:

W_1 = weight of the crucible,
W_2 = weight of crucible and waste at room temperature (rt), and
W_3 = weight of crucible and waste after drying at ≥1000°C.

7.3.1 The $(\text{wt\% LOH})_{\geq 1000°\text{C}}$ gives the total amount of volatiles to be expected in the off-gas in weight percent.

7.4 *Cation Analyses*—Calcine a few grams of waste at ≥1000°C and follow the dissolution methods outlined in 6.3.

7.5 *Anion Analyses*—Calcine a few grams of waste at ≥1000°C and follow the dissolution methods outlined in 6.4. Speciation of volatile anions such as $CO_3^=$, NO_3^-, and NO_2^- will not be possible as this method gives the total volatiles (wt%). Depending on the calcining temperature, F^-, Cl^- and $SO_4^=$ may or may not be present.

7.6 *Accuracy Assessment by Mass Balance* (100 ± 5 wt%)—Follow methods outlined in 6.11.1. If an oxide mass balance of 100 ± 5 wt% cannot be achieved, repeat analysis, try Waste Analysis Method C or Method A.

8. Test Method C

8.1 Waste analysis Method C uses wastes dried at 105°C to determine the weight percent solids and wastes dried at ≥1000°C for cation analysis. The waste analyses strategy for Method C is given in Fig. 5.

8.2 *Weight Percent Solids*—Same as section 7.2.

8.3 *Loss-On-Heating and Off-Gas System Loading*—Same as section 7.3.

8.4 *Cation Analyses*—Weigh out 10 g of waste. Add a known amount of B_2O_3 to the waste and fuse into glass at ≥1000°C until a constant weight is achieved. Up to 5 g of B_2O_3 can be added per 10 g of waste. Follow dissolution and analytic methods outlined in 6.3.

8.5 *Anion Analyses*—Weigh out 10 g of waste. Add a known amount of B_2O_3 to the waste and fuse into glass at ≥1000°C until a constant weight is achieved. Up to 5 g of B_2O_3 can be added per 10 g of waste. Follow the dissolution methods outlined in 6.4. Speciation of volatile anions such as $CO_3^=$, NO_3^-, and NO_2^- will not be possible as this method gives the total volatiles. Depending on the calcining temperature, F^-, Cl^- and $SO_4^=$ may or may not be present.

8.6 *Accuracy Assessment by Mass Balance* (100 ± 5 wt%)—Subtract the amount of B_2O_3 added in step 8.4 from the amount of B_2O_3 measured in the waste glass. Follow the methods outlined in 6.11.1. If an oxide mass balance of 100 ± 5 wt% cannot be achieved, repeat analysis, try Waste Analysis Method B or Method A.

9. Precision and Bias

9.1 No statement is made about the precision and bias of the individual test methods used to determine the cation, anion, and volatile constituents of a waste. The precision and accuracy of these methods are given in the test methods referenced in

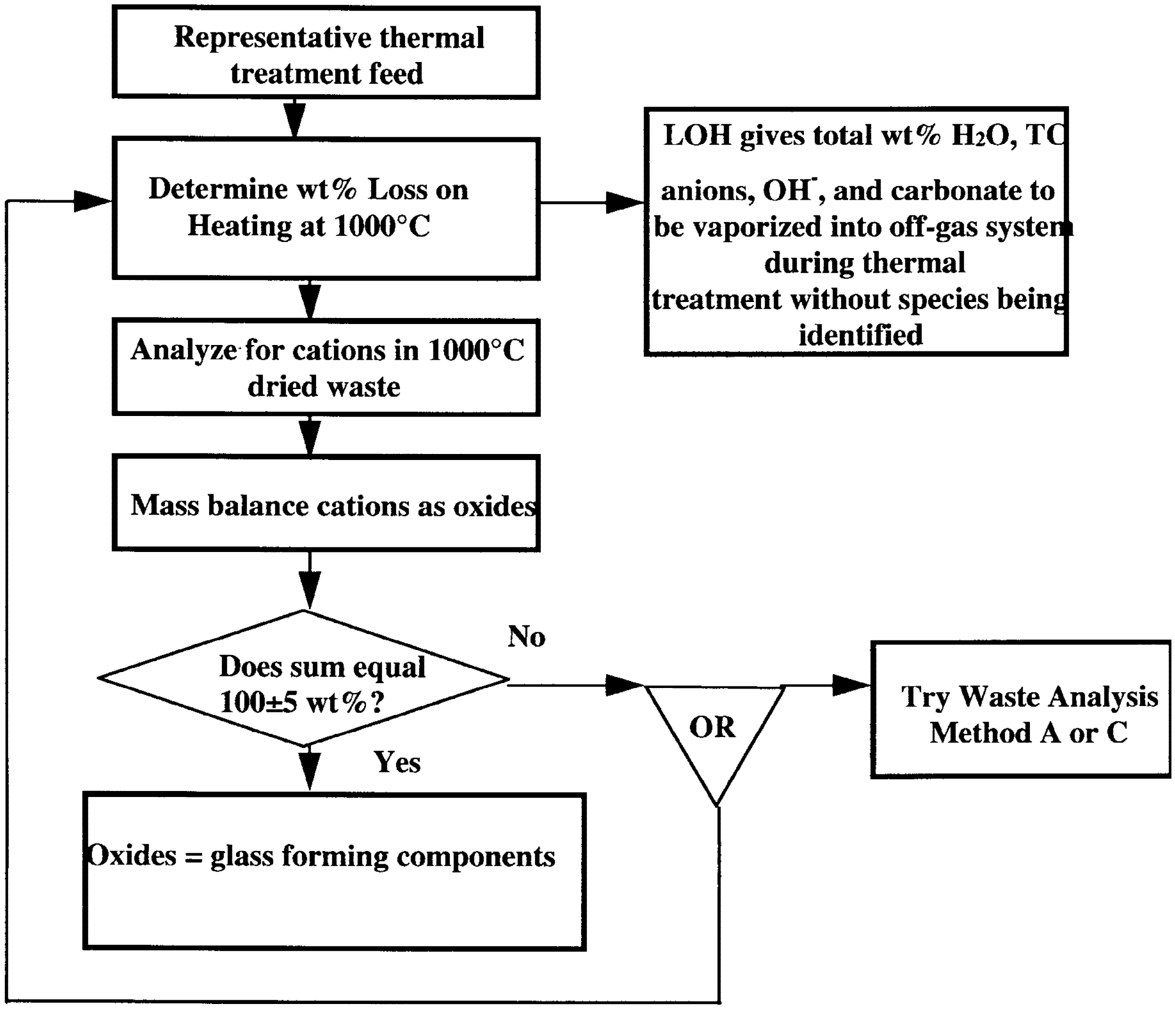


FIG. 4 Waste Analysis Method B

this guide. Since multiple test methods must be used to achieve a complete waste analysis, a method to determine the accuracy of the combined analyses to within 100 ± 5 wt% are given in 6.11 for Test Method A, in 7.6 for Test Method B, and in 8.6 for Test Method C.

10. Keywords

10.1 accuracy assessment; mass balance; thermal treatment; waste analyses

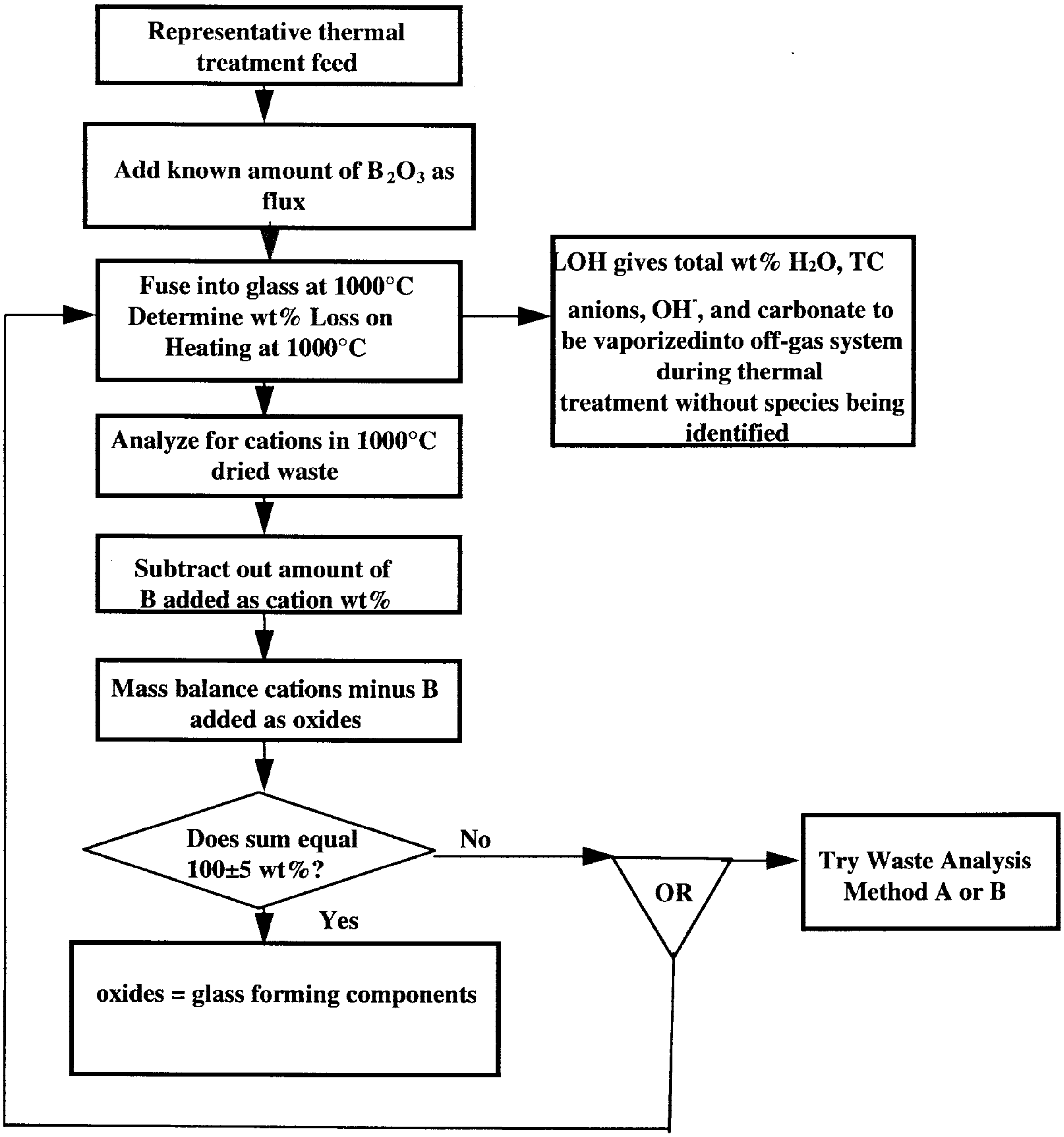


FIG. 5 Waste Analysis Method C

APPENDIX

(Nonmandatory Information)

X1. CHOICE OF OXIDE SYSTEMS FOR FORMATION OF GLASS WASTE FORMS

X1.1 When waste analyses from Methods A, B, and C are converted to an oxide basis, the use of phase diagrams such as those shown in Figs. X1.1-X1.3 can be used to determine the best glass forming system for the waste of concern. These examples are not considered inclusive of all potential oxide systems that can be used for thermal treatment of waste since additional factors such as cost and compatibility of the molten waste plus glass forming oxides with the thermal treatment unit materials of construction must be considered. However, the diagrams illustrate how simple waste form compositions can be achieved by adjusting the waste plus glass former composition to take advantage of the common glass forming constituents, for example, Si, Al, Na, and Ca, already in the waste material.

X1.2 The tolerance of glass based waste forms for many different kinds of waste, plus the common glass constituents contained in many wastes enables glass waste forms to be very accommodating to process chemistry variation. During the vitrification process the waste species become bonded in the glass or crystalline phases as oxide components. Hence all diagrams are given in oxide weight percent (wt%) in order to illustrate the composition range(s) in which glass waste forms will most likely form. The glass forming regions are shaded in Figs. X1.1-X1.3. Formulation of waste glasses outside the shaded areas will result in glass ceramics and/or glass slag waste form formation.

X1.3 Borosilicate glasses are alkali-aluminosilicate type glasses which are fluxed with boron (Fig. X1.1) and can accommodate up to ~12 wt% Fe_2O_3 and other transition metals. The generally low alumina content of these waste forms and the presence of boron lowers the melt viscosity and hence the processing temperature to ~1150°C relative to that of the aluminosilicate glasses which melt in excess of 1400°C. The lower melt temperature of borosilicate glass waste forms allows for greater retention of volatile hazardous and radioactive species than higher temperature glass waste forms. Borosilicate glasses are currently being used in the US, UK, Germany, France, and Japan, to stabilize high level radioactive wastes. Other countries such as Switzerland have accepted this form of stabilization for waste arising from the reprocessing of their fuel abroad. Belgium had been using borosilicate glass for radioactive waste disposal until recently.

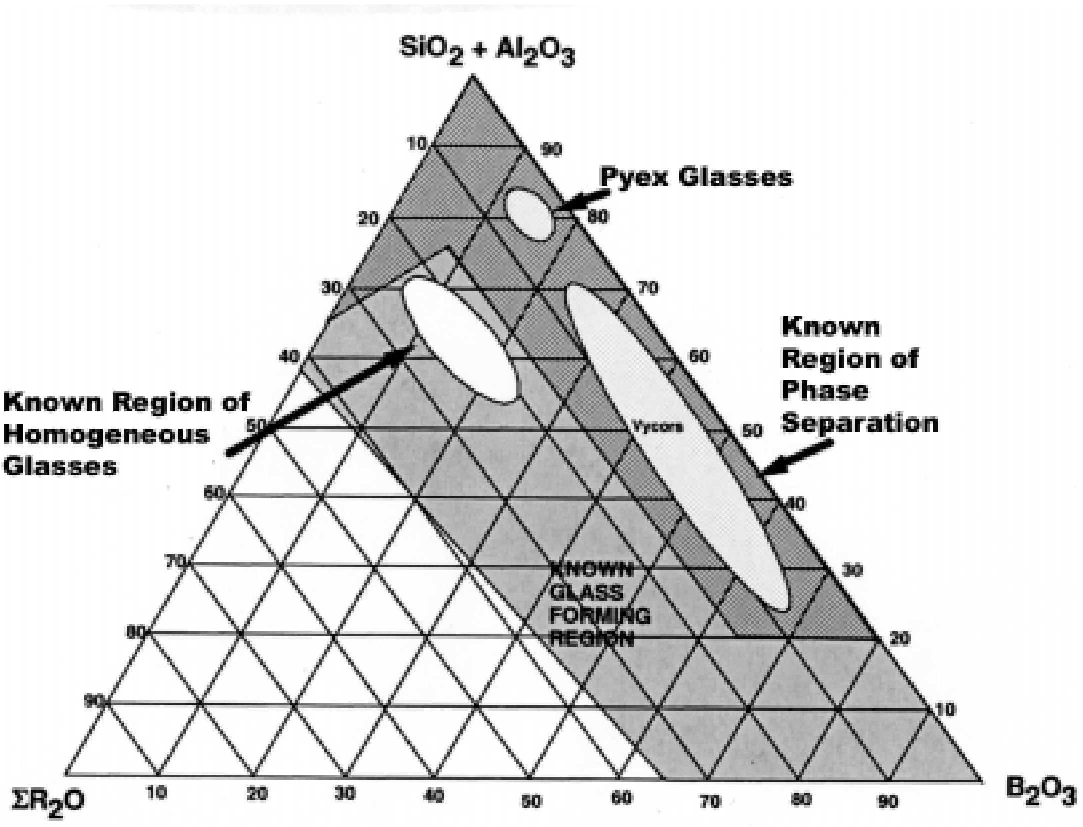
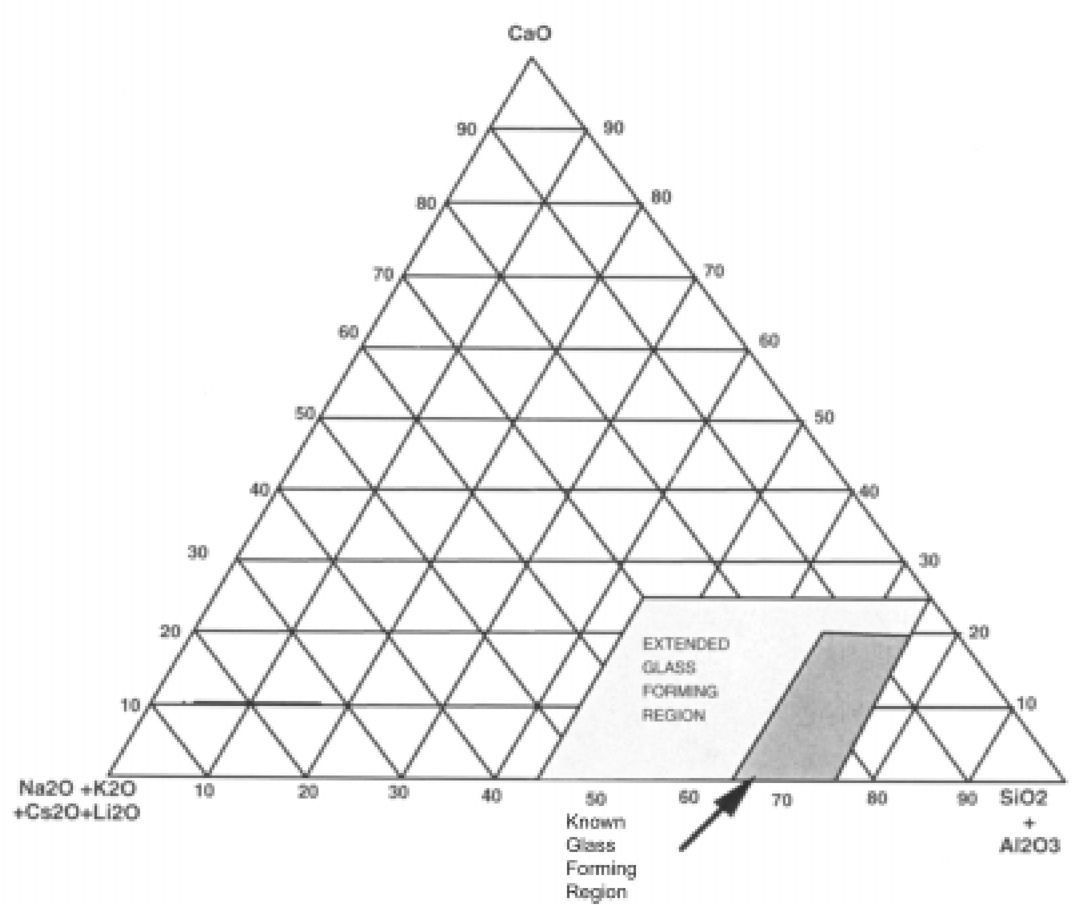


FIG. X1.1 Ternary Diagram of the Alkali-borosilicate Oxide System Demonstrating the Compositional Regions of Common Glass Formation and Usage are Located



NOTE—The lighter shaded area indicates the extended glass forming region demonstrated by Jantzen (Jantzen, C. M., Pickett, J. B., and Ramsey, W. G., "Reactive Additive Stabilization Process (RASP) for Hazardous and Mixed Waste Vitrification," *Proceed. Second Inter. Symp. on Mixed Waste*, A. A. Moghissi, R. K. Blauvelt, G. A. Benda, and N. E. Rothermich (Eds.), Am. Soc. Mech. Eng., 1993, pp. 4.2.1-4.2.13.) to form in the presence of high Fe_2O_3 and ZnO containing wastes and using the RASP™ vitrification technology.

FIG. X1.2 Ternary Diagram Showing the Region of Glass Formation (Darker Shaded Area) in the Soda-Lime-Silica (SLS) Oxide System

X1.4 The Soda-lime-silica oxide system is shown in Fig. X1.2. Soda-lime-silica (SLS) glass is known to be extremely tolerant of heavy metals waste constituents.[23,25] SLS glass formulations have been used for In-Situ Vitrification (ISV) to solidify contaminated soils[26] and a barium (Ba) analog (Soda-Baria-Silica) glass has been used at Fernald to vitrify residues from uranium ore processing that contain large contents of uranium, radium, and lead.[27,28] For Fernald waste solidification the barium rich glass was chosen due to the high barium content of the waste. SLS glasses were also successfully

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[25] Jantzen, C. M., Pickett, J. B., and Ramsey, W. G., "Reactive Additive Stabilization Process (RASP) for Hazardous and Mixed Waste Vitrification," *Proceed. Second Inter. Symp. on Mixed Waste*, A. A. Moghissi, R. K. Blauvelt, G. A. Benda, and N. E. Rothermich (Eds.), Am. Soc. Mech. Eng., 1993, pp. 4.2.1-4.2.13.

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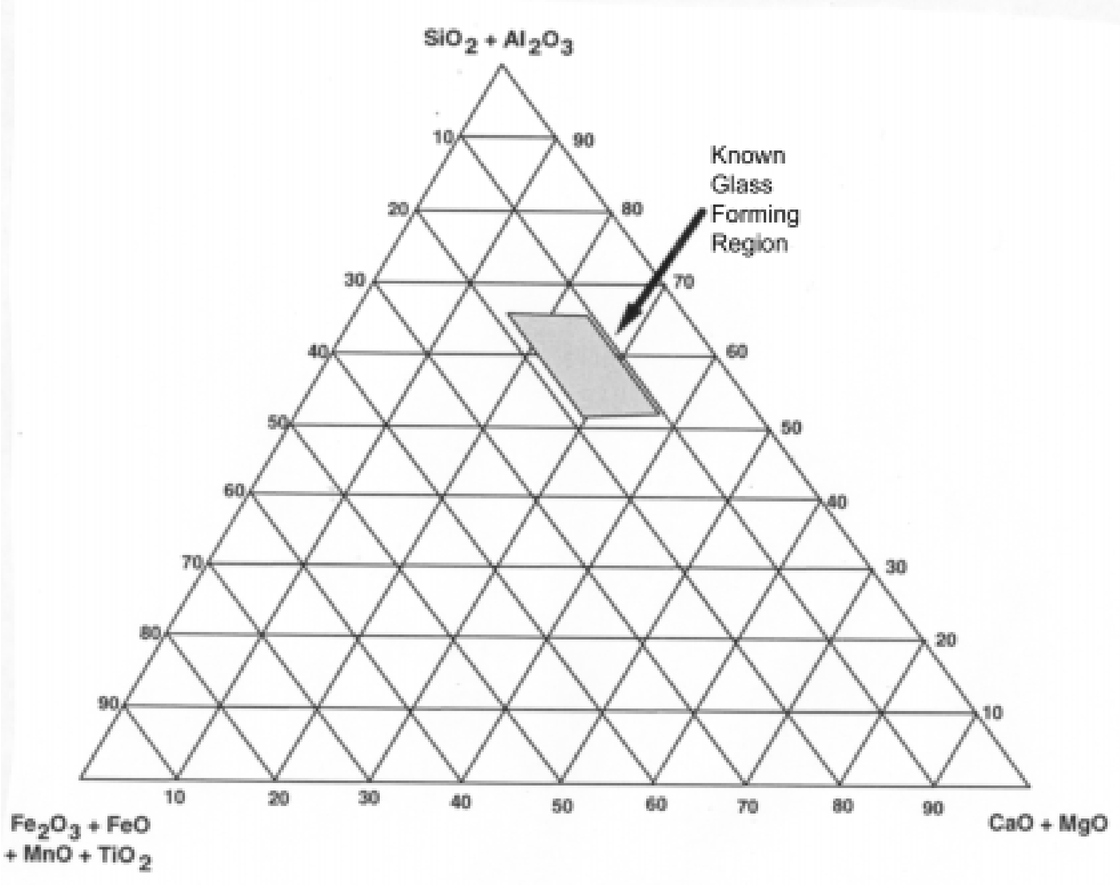
[27] Janke, D. S., Chapman, C. C., and Vogel, R. A., "Results of Vitrifying Fernald K-65 Residue," *Nuclear Waste Management IV*, G. G. Wicks, D. F. Bickford, and L. R. Bunnell (Eds.), Ceramic Transactions, Vol 23, American Ceramic Society, Westerville, OH, 1991, pp. 53-61.

[28] Jantzen, C. M., and Pickett, J. B., "Vitrification of Simulated Fernald K-65 Silo Waste at Low Temperature," *Environmental Issues and Waste Management Technologies in the Ceramic and Nuclear Industries*, Vol IV Ceramic Transactions, v. 93, J. Marra and G. T. Chandler (Eds.), American Ceramic Society, Westerville, OH, 1999, pp. 203-212; Jantzen, C. M., and Pickett, J. B., "Vitrification of Simulated Fernald K-65 Silo Waste at Low Temperature," *U.S. DOE Report WSRC-TR-97-0061*, Rev. 1, Januray 14, 1999.



NOTE—Glass forming composition limits determined from Volf, Table 114 containing the composition limits of basaltic fiber glasses (Volf, M. B., "Technical Glasses," Sir Issac Pitman & Sons, Ltd, London 1961, p. 465.)

FIG. X1.3 Ternary Diagram Showing the Region of Glass Formation (Shaded Area) in the Basalt Glass Ceramic System

fabricated from reactive sodium (Na) metal formed and contaminated during efforts to develop sodium-cooled fast breeder nuclear reactors.[29]

X1.5 The basalt glass forming system shown in Fig. X1.3 has been used to stabilize high Fe_2O_3 wastes from incinerators. Incinerator slag[30] and nuclear waste incinerator ash[31] containing little or no alkali has been mixed with a common rock, basalt, and basalt glass or glass ceramics have been fabricated at temperatures in excess of 1300 to 1400°C (Fig. X1.3). The basalt glass ceramic system was also used for cleanup of UO_2 fuel rods from Three Mile Island.[32] While the high temperature of basalt glass ceramics was appropriate for the remediation of UO_2 waste, the high temperatures can cause excessive volatility of some hazardous waste species and, therefore, basalt glass has not become widely used for stabilization of wastes containing hazardous volatile constituents.

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[29] Kumar, R., and Helt, J. E., "Improved Treatment/Disposal of Reactive Metals. Phase II: Technical Research and Development," *U.S. DOE Report ANL-91/21*, Argonne National Laboratory, Argonne, IL, May, 1991.

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