Vitrification of Mixed Wastes, the Good, the Bad, and the Ugly

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ABSTRACT

While vitrification may be quite applicable to some materials such as high level wastes that contain contaminants warranting an extremely high durability product, potential users should proceed with great caution when considering the technology for most other radioactive applications. Vitrification could be applicable to mixed low level or transuranic wastes because of the potential benefits of volume reduction, but is not attractive for low level wastes because such treatment is neither required nor cost-effective. Unfortunately, shipping and disposal costs do not have a linear relationship with absolute volume reduction, and greater volume reduction does not necessarily equate to lower overall costs. Low temperature stabilization technologies may yield greater final waste volumes, but simple stabilization processes with broad feed tolerances have the potential to reduce life-cycle costs substantially.

To consistently produce a high quality glass requires a high degree of control over process chemistry and conditions. Though all thermally stable materials will melt with adequate energy input, it cannot be assumed that the product will necessarily meet performance specifications. Management of melter feed material and the proper allocation of additives is a complex operation. While vitrification of TRU or MLLW would not require the exacting standards necessary for HLW, many potential feed and melt characteristics, such as salt, organic, and metal content, and viscosity and basicity limit the processing envelope for maintaining safe, reliable operation, and to produce an acceptable glass. A well operated vitrification plant with high reliability and consistent, well-characterized inorganic feed has the potential to produce a high-density, durable product ideal for containment of particularly toxic long-lived species, but the relatively strict process requirements preclude broad cost-effective application to mixed low level and TRU wastes.

INTRODUCTION

Vitrification of waste can yield a highly durable product at essentially theoretical density, thus offering the potential for maximum volume reduction. In addition, moisture and organic matter are eliminated, thus eliminating the potential for hydrogen generation in a waste matrix contaminated with transuranic elements. Due to the amorphous nature of glass, virtually any thermally stable compound can be incorporated, though the loading capacity for some compounds may be limited by glass chemistry and durability requirements. To consistently produce a high quality glass requires a high degree of control over process chemistry and conditions.

As described below, what was once conceived as potentially a “kick-and-roll” concept has proven to be elusive. Even with excellent control of the process, certain consequences typical of high-temperature processes such as metal and radionuclide volatility, and corrosion of refractory and electrode materials must be addressed. For melters treating Resource Conservation and Recovery Act (RCRA) regulated organic contaminants, the likelihood of permitting as an incinerator must also be considered. Though state-of-the-art engineering practice and atmospheric protection system design can address most of the concerns vitrification processes have in common with more traditional incineration, satisfactory implementation is quite complex.

Vitrification development has continued for years to produce ever more durable glasses and reliable melter designs for high level waste (HLW). The HLW streams being processed are liquids or finely divided solids (sludges and salts), and are some of the most thoroughly characterized materials in the DOE complex. Much of this development has continued due to the lack of hard performance requirements for radioactive waste products in the United States. Borosilicate glass formulations developed for HLW produce glasses expected to contain long-lived radionuclides for many thousands of years. In the absence of a regulatory standard, glass formulation has culminated with the highly durable glasses now being produced at West Valley and the Savannah River Site. Extrapolation of this experience to mixed low level or transuranic (TRU) wastes, however, means consideration of a much wider variety of materials, and is generally only justified by the potential for volume reduction, which could reduce shipping and disposal costs.

This paper summarizes the major advantages and disadvantages of applying vitrification technology to mixed low level and TRU wastes.

REGULATORY ENVIRONMENT

The American regulatory structure obviously has a strong impact on technology selection for radioactive wastes. Vitrification is the treatment standard for high level wastes(1), though a permanent repository has yet to be sited, thus the final performance specifications can only be guessed. Conversely, disposal of TRU contaminated wastes containing many of the same long-lived radionuclides, though generally at much lower levels, is set for the Waste Isolation Pilot Plant (WIPP), but treatment standards are still unresolved. While materials bearing only TRU contamination may go into the WIPP facility untreated under the Land Withdrawal Act; the State of New Mexico may yet require treatment to meet Land Disposal Restrictions (LDRs) for those TRU wastes contaminated with RCRA regulated materials. Discerning between these two classes of TRU wastes may be so problematic that treatment may be done for all TRU material potentially containing RCRA contaminants. Meanwhile, low level wastes (LLW is radioactive only, and not TRU or HLW), primarily soils and debris contaminated with relatively short-lived fission and activation products, are considered low risk and routinely interred in landfills without treatment. However, mixed low-level wastes, LLW containing RCRA regulated contaminants must be treated to meet LDRs before disposal. In any event, methods specified by the Environmental Protection Agency for meeting LDRs for chemical constituents do not require vitrification.

In summary, vitrification was dictated by congressional mandate for HLW to ensure product durability, but is not required any other radioactive wastes. Vitrification could still be applicable to mixed low level or TRU wastes requiring treatment because of the potential benefits of volume reduction, but is not attractive for LLW because such treatment is neither required nor cost-effective.

VOLUME REDUCTION

Is vitrification warranted on the basis of volume reduction during stabilization alone? In theory, it certainly could be. A well operated vitrification plant with high reliability and consistent, well characterized feed has the potential to produce a high-density, durable product meeting all NRC guidance, EPA and State regulations, and many, if not all, waste form concerns identified by interested members of the public. However, with the additional realities of container weight and integrity requirements, the potential for required permitting as an incinerator, and the wide variability in chemistry and characterization capabilities for mixed waste, one quickly finds that cost-effective broad application may be superceded by incineration or low-temperature oxidation technologies and stabilization with advanced grout formulations. These competing technologies may generate larger disposal volumes, but the life-cycle costs are frequently competitive with the life-cycle costs of vitrification.

Unfortunately, shipping and disposal costs do not have a linear relationship with absolute volume reduction. Container weight limits preclude filling standard 55-gallon drums full with slag(2), and for TRU wastes, Department of Transportation requirements preclude shipping the entire 14-drum capacity of the TRUPACT II container at maximum container weight(3). In addition, pouring molten material into a standard drum may cause it to lose its shipping integrity, requiring an over-pack, thus negating much of the volume-reduction and incurring the additional expenses of repackaging. Some of these disadvantages can be mitigated by using rectangular container shapes as was done for the Transportable Vitrification System (TVS) demonstrated at Oak Ridge(4). Radionuclide inventory may also be an issue; driving off thermally labile compounds and evaporating water has the net effect of concentrating waste, which may readily place it into a new classification, particularly with trace level TRU contamination planned for commercial disposal(5). This may increase life-cycle costs or even preclude disposal of the waste by concentrating the material beyond the permitted waste acceptance criteria (WAC).

An excellent analysis by Schwinkendorf and Cooley(6) showed the transition in cost amongst competing technologies for several process evaluation variables. Though semi-vitreous monoliths had many cost advantages, Portland cement was a strong competitor under some circumstances, and advanced grout-like materials such as phosphate bonded ceramics were quite competitive on a cost basis under many conditions.

As is the case with all evaluations, the results depend upon the assumptions used as a basis. On one end of the vitrification spectrum is high-temperature plasma-fired melting to produce a glassy slag, which may be sufficient to pass Toxic Characteristic Leach Procedure (TCLP) requirements with non-waste additives required only to meet processing requirements. Though plasma temperatures are sufficient to melt or destroy almost anything found in DOE wastes, refractory and torch durability, as well as volatility of many compounds limits plasma-system reliability. At the opposite end of the range of DOE supported vitrification technologies are joule-heated melters, including those used to produce the extremely durable glasses for HLW stabilization. However, high quality borosilicate glass is produced at the cost of waste loading, typically limited to about 30 wt%, and stringent feed constraints that limit broad application to mixed wastes. Similarly, non-vitrification technologies vary from standard Portland cement formulations which may be limited to minimal waste loadings, to advanced grouts such as phosphate-based ceramics and fly-ash formulations, which may compete with joule-heated melters for waste loading, while offering the potential for much greater reliability than thermal systems. These relatively new grout technologies are not without challenges, requiring tailored formulation for specific contaminants, and, for organic materials, coupling with incineration, pyrolysis, or chemical oxidation. However, the simple ambient-temperature stabilization process equipment and broad feed tolerances have the potential to reduce life-cycle costs substantially. Schwinkendorf and Cooley(6) summarize the crossover in cost effectiveness depending on the selected evaluation assumptions in the analysis. System availability was found to be the primary cost driver.

PROCESS CHEMISTRY

Thus, glass is not required by regulations for TRU or MLLW, nor is it necessarily cost-effective based on volume reduction, but what if it is still desirable as a high-durability product? Vitrification may also be accepted by regulators as a basis for delisting the product after treating listed wastes. This could allow simple disposal as LLW rather than MLLW. For a consistent, well-characterized waste, particularly an inorganic matrix containing long-lived, non-degradable, highly toxic material, vitrification may be quite applicable. Where conditions warrant the technology, the user’s concerns are reduced to process chemistry and process control. Operation of the Defense Waste Processing Facility (DWPF) at the Savannah River Site (SRS) is an excellent example of the stringent quality assurance needed to guarantee the consistent durability of a glass product. Jacobs and Elder(7) summarized the system used at SRS to ensure compliance with HLW feed specifications.

Though all thermally stable materials will melt with adequate energy input, it cannot be assumed that the product will necessarily meet performance specifications. Management of melter feed material and the proper allocation of additives is a complex operation. Balancing given variables in feed chemistry, with waste loading, product durability, and reliable operation requires constant compromise. Industrial glass melters produce the same type of glass throughout campaigns. Applications of the technology to mixed TRU and LLW treatment requires flexibility. While vitrification of TRU or MLLW would not require the exacting standards necessary for HLW, many potential feed characteristics must be considered for maintaining safe, reliable operation, and to produce an acceptable glass.

Salts

The most readily explained chemical limitation for vitrification is for salts such as chlorides, nitrates and sulfates. These materials simply do not contribute to the formation of glass, nor do they readily dissolve into the matrix. Thus their content must be limited to maintain the durability of the overall matrix. These salts decompose at glass-forming temperatures and contribute to acidic HCl, NOx and SOx in the offgas, while typically leaving behind fluxing alkaline material in the melt. While this is true of any high temperature process, and the offgas can certainly be treated, occurrence in a glass melter may cause the glass to foam, leading to a low durability product. A sulfate-laden glass-foam may also cause processing problems by forming an insulating crust that may interrupt feeding, pouring, or expected heat transfer. Sulfur in feeds to the M-area melter is limited to about 1 wt%. In addition, chlorides in feeds containing toxic metals or cesium have been shown to contribute to the volatility of those elements.

Organic/Combustible Wastes

Thermal destruction of organic matter is limited by surface area and contact with oxidants. In a glass melter, destruction of organic contaminants is essentially limited to the gas-filled plenum, where volatilized material can be contacted by oxygen. Thus, the melt surface area exposed to the plenum, regardless of the total glass volume, limits the reaction of organic matter in a solid or slurry feed. Introducing oxygen through bubblers penetrating the melter below the melt line can enhance oxidation, but this added complexity may reduce melter reliability as in the case of the melter failure at Fernald(8).

In addition, regardless of the glass temperature, for broad application to combustible materials, a secondary combustor will be necessary to meet air emission standards. While a glass forming recipe can be made more oxidizing to accommodate some incidental organic contamination, or run with a steam-filled plenum to generate a syngas, a vitrification unit with a secondary combustor looks a lot like an incinerator. Considerable organic content in a melter feed can quickly cause reducing conditions that can convert metals to their elemental form adding to volatility creating separate phases, and potentially reducing overall product durability. Control of melt redox conditions is an important factor when feeding wastes including combustible constituents. For these reasons, feed to joule-heated melters producing glass to pass TCLP is nominally limited to 3-5 wt% carbon. For combustible materials, this may necessitate pretreatment such as chemical oxidation or incineration.

Free Metals

Glasses have a fairly high capacity for solubilizing and immobilizing metals. Lead crystal stemware can contain several weight percent lead with amazing durability. However, the metals must be oxidized, which again requires an adequate content of oxidants. Similar to the statement above for organic matter, a glass recipe can be tailored to accommodate some metal. One advantage over organic matter is that many metals in DOE mixed wastes are already oxidized and dissolve readily in glass. However, free metals (particulate, shavings, and debris) will not readily oxidize in a melter, and may sink to the bottom, coalescing to form a separate phase. Though a melter can be designed to accommodate this phase, it presents the potential hazard of shorting across electrodes, and may be very difficult to tap without pouring glass as well. Maintaining the proper redox conditions is essential to safe operation. One of the contributing causes cited for the Fernald melter failure was lead reduction at the expense of the molybdenum dioxide bubblers, producing elemental lead[5]. The lead is then believed to have corroded refractories, leading to loss of containment and melter short-circuiting, finally ending in loss of the melter.

Melt Viscosity

The molten glass must be pourable to decant it from the melter. Any waste can be made pourable with sufficient addition of fluxing material such as sodium and lithium oxides, but then additional glass formers may be necessary to result in a sufficiently durable glass to meet performance requirements. This dichotomy is what limits the waste loading in borosilicate products. The viscosity requirement has driven processing temperatures up to the operating limit of practical materials of construction for contact refractories and electrodes. While many sludges from waste water treatment contain sufficient alkaline fluxing material to result in reasonable waste loading within the operating temperature range of joule-heated melter designs, this is not true of most soils. The high silica content of soil creates a very viscous melt requiring substantial dilution, or much higher temperatures. This is one reason why plasma systems were explored under programs designed to evaluate and develop systems for treating wastes to be retrieved from radioactive waste landfills such as the Radioactive Waste Management Complex at the Idaho National Engineering Laboratory(9). Thus soil feeds to joule-heated melters will be more an exception than rule. In contrast, making a glass too fluid with fluxing material may challenge containment using refractory brick construction. Both the Transportable Vitrification System at Oak Ridge(10) and the M-Area melter(11) at Savannah River failed when the melt viscosity dropped to a critical level, seeping through joints between bricks, causing melter short-circuiting and loss of containment. Adding cooling systems outside the containment refractories to freeze leaking material and using cast instead of jointed materials are modifications designed to address these problems.

Melt Basicity

A glass melt contains basic and acidic components. Matrix formers are generally acidic trivalent ions such as silicon and aluminum, while fluxes are generally basic monovalent ions such as sodium and lithium. The balance in any particular melt results in a characteristic melt basicity, which has a direct impact on corrosion of glass-contact refractories. A melter designed for operation with a highly acidic glass, will probably not have as great a design life if operated under basic conditions. If waste feeds are highly variable, such as mixed waste debris or ash from, and the melt basicity alternates between basic and acidic, it will be very difficult to adequately predict refractory life.

CONCLUSIONS

While vitrification may be quite applicable to some wastes containing contaminants that warrant an extremely high durability product, potential users should proceed with great caution when considering the technology for most TRU and mixed waste applications. Vitrification technology can produce a highly durable product under carefully controlled conditions with well characterized, consistent feeds. Under the right combination of technology selection constraints it may also be quite cost-effective due to the extreme volume reduction obtainable by melting, particularly for high-volume, uniform wastes. One example is treatment of wastewater treatment sludges, which offers the potential for significant volume reduction by driving off the substantial water content and melting the high silica, high alkaline-earth contents typical of those wastes. A simple cost comparison can evaluate the benefits of vitrification versus evaporation and followed by stabilization with a chemical binder.

In addition, a highly durable glass product may be desirable regardless of cost due to highly toxic, long-lived constituents in the waste or delisting considerations. However, for applications to new waste streams, technology evaluation requires careful consideration of waste chemistry before extrapolating from prior experience. Interaction of materials of construction with the waste melt (e.g. redox conditions and melt basicity) may lead to unforeseeable consequences. Thus materials of construction must be chosen for the intended waste feed compositions. Wastes containing significant amounts of carbon, salts, free metals, lead, or mercury compounds may require pretreatment or blending prior to vitrification. Consideration of vitrification technology as a “kick and roll” concept, wherein drums of waste are literally fed whole to a melter with only minor characterization is clearly not economically possible for broad application to diverse TRU or mixed wastes under the current framework of environmental regulation and safe engineering practice.

REFERENCES

1. Code of Federal Regulations 40 CFR 264.40 “Treatment Standards for Hazardous Wastes”.

2. 49 CFR 178.504 "Standards for Steel Drums".

3. Waste Acceptance Criteria for the Waste Isolation Pilot Plant, April 1996, Section 3.2.2.2 "TRUPACT II Waste Requirements", DOE/WIPP-069, Rev 5, Change Notice #2, February 1998.

4. “Performance Test Report for the Transportable Vitrification System at the East Tennessee Technology Park,” K/WM-182, Lockheed Martin Energy Systems, Inc., East Tennessee Technology Park, May 1997

5. C. R. Cooley, DOE/EM-50, W. E. Schwinkendorf, and T. E. Bechtold, Lockheed Martin Idaho Technologies Company (INEEL), "Integrated Process Analysis of Treatment Systems for Mixed Low Level Waste," Technology: Journal of the Franklin Institute, Vol. 334A, No. 2-6, 1997, pp. 303-325.

6. W. E. Schwinkendorf Lockheed Martin Idaho Technologies Company (INEEL) and C. R. Cooley, DOE/EM-50, “Costs of Mixed Low-level Waste Stabilization Options”, presented at Waste Management ’98, Tucson, AZ, March 1-5, 1998.

7. Jacobs, R. A. and Elder, H. H., Westinghouse Savannah River Company, “Feed Acceptance for the Defense Waste Processing Facility at the Savannah River Site (U)," presented at the Spring National Meeting of the American Institute of Chemical Engineers, New Orleans, LA, March 8-12, 1998.

8. "Vitrification Pilot Plant Melter Incident: Final Report," 40100-RP-0019, February 1997.

9. T. L. Eddy, P. C. Kong, B. D. Raivo, and G. L. Anderson, EG&G Idaho, “Thermal Processing System Concepts and Considerations for RWMC Buried Waste,” Idaho National Engineering Laboratory, EGG-WTD-10058, February 1992

10. “Supplement to the Transportable Vitrification System (TVS) Leak Incident Report: Assessment of Design Modifications, Disassembly Evaluation, and Melter Rebuild,” K/WM-149/8, Lockheed Martin Energy Systems, Inc., East Tennessee Technology Park, May 1997

11. B. W. Bowen, “SRS M-Area Sludge Vitrification Project”, GTS Duratek, May 1998 Update