Prospects for Vitrification of Mixed Wastes at ANL-E

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Summary

This report summarizes a study evaluating the prospects for vitrification of some of the mixed wastes at ANL-E. This project can be justified on the following basis:

- Some of ANL-E's mixed waste streams will be stabilized such that they can be treated as a low-level radioactive waste.
- The expected volume reduction that results during vitrification will significantly reduce the overall waste volume requiring disposal.
- Mixed-waste disposal options currently used by ANL-E may not be permissible in the near future without treatment technologies such as vitrification.

Preliminary laboratory work with surrogate waste streams indicates that waste evaporator and concentrator bottom sludge, as well as high efficiency particulate air (HEPA) filters, can be vitrified under conditions readily achieved with commercial vitrification technology. The vitrified waste products were homogeneous and had viscosities favorable for processing. This work provides an experimental basis for further investigating and implementing vitrification as a candidate mixed-waste treatment technology. At this point, we have concluded that a vitrification system can handle clearly defined mixed waste streams at ANL, if the process is not constrained by the use of glass-forming additives to solubilize hazardous elements.

Volatility of metals (hazardous and radioactive) was also considered. The hazardous elements in the actual mixed-waste streams (Ag, As, Ba, Cd, Cr, Hg, Se, and Pb) are known to be soluble in silicate glasses at the concentration levels anticipated for the ANL-tailored vitrified product. Their volatilities need to be experimentally confirmed. The elements of most concern include Hg, Cd, and As. These elements can be controlled with the use of Hg traps, scrubbers, and HEPA filtration as part of the off-gas system. The final off-gas configuration specific to ANL's needs will be determined with the commercial firm providing the vitrification system.

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Analyses of the ANL waste streams show that the primary off-gases produced during vitrification include compounds of SO_x , NO_x , and CO_2 . These compounds are routinely treated in vitrification systems. The composition of the melter feed can be adjusted to control some of the off-gases produced, if necessary. Initial correspondence with the Illinois EPA has indicated that a vitrification system would not be subject to the same regulations and scrutiny as an incineration unit. Instead, it will be considered a thermal treatment unit. At this point, it appears that off-gas problems should be solvable with commercial technology.

The cost benefits of vitrification appear to be substantial. The volume reduction of the sludge waste is anticipated to range up to a factor of 70%, while a volume reduction of a factor of 100 is expected for HEPA filters. Volume reductions will be maximized as the waste loading is optimized through waste blending to minimize the addition of glass-forming fluxes. This aspect can be determined when all the waste streams to be vitrified are identified. The disposal costs of low-level radioactive wastes are lower than those of mixed waste by a factor of two, although on-site mixed waste treatment may be mandated in the future.

In conclusion, the prospects for use of vitrification of mixed wastes at ANL are excellent. (1) The practical treatment feasibility has been demonstrated in the laboratory with surrogate feeds. (2) Glass chemistry indicates that all Resource Conservation and Recovery Act (RCRA) metals can be incorporated into glass melts. (3) Waste streams with unusually high RCRA metal contents can be accommodated by adjusting the feed stream to solubilize those elements. (4) Commercial off-gas systems can treat the gases expected to be produced during vitrification. The economics suggest that annual cost savings may be many hundreds of thousands of dollars as a result of volume reduction and conversion of mixed waste to low-level waste.

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Prospects for Vitrification of Mixed Wastes at ANL-E

Introduction

Mixed wastes have become extremely difficult to dispose. The only DOE site that currently accepts mixed waste (Hanford) may close in the near future or require that wastes be treated to eliminate their hazardous components. In addition, the relatively high cost of disposing mixed wastes (approximately \$150/ft³ versus \$70/ft³ for low-level radioactive wastes) provides additional incentive to minimize the amounts of mixed waste for disposal. One strategy for dealing with some of the mixed waste streams at ANL employs vitrification technology. The primary goals of using vitrification are to

- (1) convert the mixed waste to a low-level radioactive waste form that is stable and leach resistant, thereby making it acceptable for shallow land burial; and
- (2) reduce the waste volume, further lowering the disposal costs.

Vitrification is currently under consideration as a treatment technology for a number of wastes streams throughout the DOE complex. Vitrification has been designated the best available demonstrated technology for the treatment of high-level radioactive waste (HLW). However, the strategy for vitrification treatment of HLW has focused on the need to produce a homogeneous durable product that will isolate radioelements from the biosphere for thousands of years. The proposed mixed-waste vitrification for ANL will concentrate on forming a stable, leach-resistant glass product while achieving maximum volume reduction. The HLW vitrification program has been less concerned with volume reduction. Vitrification technologies are relatively mature; however, their abilities to treat mixed wastes have not been explored in great detail.

A vitrification program at Fernald, Ohio, is completing construction and installation of a pilot-scale joule-heated melter (300 kg/day nominal capacity). The project, entitled the Minimum Additive Waste Stabilization (MAWS) Program, will evaluate the feasibility of vitrification of mixed wastes as a remediation technology for site clean up. The objective of this program is to demonstrate a MAWS system which will treat and blend multiple waste streams. The principle of using vitrification at Fernald has previously been demonstrated with smaller scale (10 and 100 kg/day nominal capacity) melters, and economic analyses indicate that the cost savings there will be in the range of hundreds of millions of dollars. The volume of mixed wastes at

ANL-E is smaller than that at Fernald, but the savings per unit of waste could be similar.

Vitrification programs with microwave technologies are also being evaluated for treatment of high-level radioactive wastes at Savannah River, low-level radioactive wastes at Rocky Flats, and transuranic wastes at Oak Ridge. Vitrification at Rocky Flats has achieved up to 80% volume reduction compared to grouting treatments. Similar scale volume reductions will be sought in the proposed program at ANL-E.

This report summarizes what we found in studying ANL-E mixed-waste streams for vitrification. In particular, we present

- (1) Assessments of whether the toxic metals in the waste streams pose any special problems or hazards during vitrification.
- (2) Known or anticipated compositional limits to vitrification for the waste streams considered.
- (3) Known or anticipated concerns with respect to volatility of metal or off-gas concerns.
- (4) Estimates of the economic benefits expected from treating ANL's mixed wastes with vitrification.
- (5) Identification of specific ANL mixed-waste streams that can be treated by vitrification.

Mixed-Waste Streams

Four candidate mixed-waste streams are considered for this report, referred to as evaporator concentrator bottoms sludge, Cu-sulfide sludge (resulting from other mixed-waste treatment), storage tank sludge, and HEPA filter media. Each waste stream is mixed waste by virtue of its failure to pass the Toxic Characteristic Leaching Procedure (TCLP) test. The approximate concentration of each waste stream is presented in Table 1. Evaporator bottoms sludge consists primarily of sodium salts and approximately 50 wt % water. Evaporator sludge bottoms are considered mixed wastes because of the presence of some radioactive elements and the presence of trace (a few thousand ppm) metals, including Ag, As, Ba, Cd, Cr, Hg, Se, and Pb. The Cu-sulfide sludge consists primarily of CuS, with minor amounts of Ca phases. The HEPA filters consist primarily of borosilicate glass. These particular HEPA filters are treated as

mixed wastes because of the presence of Pb along with radioactive elements. The availability of HEPA filters as a candidate for vitrification did not become apparent until late in this preliminary study, and this waste stream has not been used in any crucible studies. However, note that the chemistry of HEPA filters, including their contamination, is compatible for vitrification treatment.

Table 1. Reported Compositions of ANL-E Mixed Waste Streams. All values are reported in wt%. Evaporator bottoms sludge and Cu-sulfide sludge compositions obtained from J. Hutter (CMT) and the HEPA filter compositions obtained from H. No (WMO).

Constituent	Evaporator Bottoms Sludge	Cu-Sulfide Sludge	Storage Tank Sludge	HEPA filters
SiO ₂	0.1			57.0 - 69.0
Na ₂ O	36.0			8.0 - 12.5
B ₂ O ₃	0.1			4.5 - 11.0
Al ₂ O ₃				3.0 - 7.0
CaO	0.3			2.0 - 7.0
BaO				< 5.5
MgO	0.8			< 4.5
ZnO				< 4.5
K ₂ O				< 3.0
F ₂	0.4			< 1.0
Fe ₂ O ₃				< 0.2
CuS		93		
CaS		6		
Ca(OH) ₂		1		
Li ₂ O	0.1			
SO ₄ ²⁻	14.4			
NO ₃ ⁻	4.2			
NO ₂ ⁻	5.2			
HCO ₃ ⁻	27.2			
Cl ⁻	8.1			
Carbonaceous Material			25	
Ash			66	
Other	3.1		9	
Total	100	100	100	100

Technical Concerns

The technical concerns expressed by WMO for vitrification of mixed wastes at ANL-E include the following:

- (1) Can the mixed-waste streams be vitrified, resulting in a waste form that passes the TCLP test, and thus, is no longer considered a mixed waste?
- (2) What are the realistic concentration levels of hazardous constituents that can be handled by a vitrification system?
- (3) Are there any indications that operation of a vitrification system would not be allowed by agencies such as the EPA, State of Illinois, etc.?
- (4) Can the expected off-gases be handled by off-the-shelf systems?
- (5) Are there vitrification systems currently commercially available that can meet the anticipated technical specifications for the projected ANL-E system including capacity and off-gas systems)?

Feasibility of Vitrification

In this preliminary study, the feasibility of ANL-E mixed wastes has been demonstrated with crucible melts. The crucible melts were performed with surrogate evaporator bottoms sludges and surrogate Cu-sulfide sludges (i.e., the sludges contained no hazardous metals). Each sludge was initially dried at 90°C, then blended with various amounts of silica sand and boric acid. The resulting blends weighed 150 g each. These additive materials were selected because of their commercial availability. The blended waste was next preheated at 500°C in a hooded oven to volatilize the SO_x, NO_x, and CO_x compounds and to avoid foaming during vitrification. The crucible was then placed in a 1200°C furnace for 1 hour. At the end of this period, the melt was removed from the furnace, and the melt viscosity was qualitatively assessed by attempting to pour the melt from the crucible. After cooling, the glasses were recovered, visually examined, and archived.

Three melt compositions were produced. The first melt (Melt #1) contained equal amounts of sodium-sludge, silica sand, and boric acid. This blend produced a clear glass with a slight yellowish tint and no visible crystallites. Melt #1 was easily poured from the crucible. This demonstration of homogeneity and good viscosity suggests that this melt composition should be considered a good candidate for the final waste form. Two other melts (Melts #2 and #3) were produced with evaporator bottom sodium-sludge, Cu-sulfide sludge, silica sand, and boric acid. However, these melts were blended in

proportions unrepresentative of any likely vitrification at ANL and, therefore, will not be discussed any further.

Melt #1 produced a glass that appeared to have completely melted, was homogeneous, and had good viscosity. Because of the preliminary nature of this study and the use of surrogate wastes to demonstrate vitrification, TCLP testing with Melt #1 was not performed. Past experience with glass durability testing for the HLW vitrification program suggests that, had Melt #1 been produced with actual hazardous wastes, the resulting glass would pass a TCLP test.

Off-Gas Considerations

Based on an analysis of the materials in the waste streams, the following off-gases may be anticipated in the vitrification system. From the evaporator bottom sludges, SO_x , NO_x , CO_2 , Hg, and lesser amounts of F and Cl can be anticipated to appear in the off-gases. The amounts of these gases and metals will depend on the waste loading in the waste form. From the Cu-sulfide sludge, SO_x compounds will be the off-gases that need to be monitored and controlled. The HEPA filter waste stream is not expected to generate any off-gases. However, once the filter is removed from the housing, small amounts of cyanide may be produced from the residual neoprene adhesive on the filter media.

Compounds of SO_x , NO_x , and CO_2 are commonly treated with off-gas systems that are commercially available. The extent that each of these compounds may need to be controlled will be experimentally estimated during the laboratory crucible studies proposed for this project.

Volatility Considerations

Volatility of metals during vitrification may need to be addressed if it is found that they are present in quantities of regulatory concern. We anticipate that most of the RCRA metals will be soluble in the designed final waste form. These metals are anticipated to be present in the waste streams at quantities less than 0.1 wt% (1000 ppm). Their concentration in the mixed feed delivered to the melter will be further reduced by the presence of additives or non-hazardous metal-bearing waste streams (~several hundred ppm). Studies of solubilities of elements in silicate glasses indicate that these concentrations of hazardous metals should be able to be vitrified in silicate glasses, as shown in Table 2. The elements that may not remain in the melt are

Hg, Cd, and As. We believe that if these elements do not remain in the melt, they can be controlled by off-gas system.

Table 2. Approximate Solubility of Some Elements in Silicate Glasses (Adapted from Volf-1984).

Solubility	Hazardous Elements in ANL-E Mixed Waste Streams	Other Elements in ANL-E Mixed Waste Streams	Other Elements Found in Silicate Glasses
< 0.1 wt%	Ag, Hg		Ar, Au, Br, H, He, I, Kr, N, Ne, Pd, Pt, Rh, Rn, Ru, Xe
1 to 3 wt %	As, Cr, Se	S, C, Cl	Sb, Sn, Tc, Te
3 to 5 wt%		Cu, Mn,	Ni, Ti, Mo, Co, Bi
5 to 15 wt%		B, F, Th	Ce, La, Nd, Pr, Ge
15 to 25 wt%	Ba	Ca, U, Na	Al, Cs, Fe, Fr, K, Li, Mg, Ra, Rb, Sr, Zn
>25 wt%	Pb	Si	P

The air-pollution control systems typically employed to control toxic metal release in off-gases address those in particulate and vapor phases [DONNELLY-1993]. Particulate fraction control is achieved with traditional particulate control devices, such as electrostatic precipitators, fabric filters, and wet scrubbers. The vapor phase fraction is controlled by cooling the off-gas and collecting the fine particulates that result. Vapor phase control devices include spray dryer absorbers, wet scrubbers, and condensing wet scrubbers.

Estimates of the efficiency of toxic metal control of an off-gas system are reported in Table 3 [DONNELLY-1993]. All of the RCRA metals found in the ANL-E mixed wastes, except for selenium, are addressed in this report. All metals can be controlled at greater than 99% efficiency, except for mercury. The Hg collector efficiency can be improved to 95% by adding an adsorption enhancer in a spray dryer absorption system or a condensing wet scrubber following a dust collector.

Table 3. Estimates of Toxic Metal Control for Hazardous Waste Incinerators
(Adapted from DONNELLY-1993).

	EPA Conservative Estimated Efficiencies	Typical Actual Control Efficiencies	Typical Range of Emissions Rates
Particulate Matter	99+ %	99.9+%	0.005-0.02 gr/dscf
Arsenic	95	99.9+	1-5 μ g/m ³
Cadmium	95	99.7	0.1-5
Chromium	99	99.5	2-10
Barium	99	99.9+	10-25
Lead	95	99.8	10-100
Mercury	85-90	40-95+	10-200
Silver	99	99.9+	1-10

Candidate Vitrification Systems

Among the methods for heating materials are joule, plasma, microwave, resistance, induction, and electric arc heating. A review of these technologies, along with their relative advantages and disadvantages was recently presented, and is reproduced in Appendix A [USEPA-1992].

Several commercial firms that offer vitrification systems for sale were contacted to estimate availability and costs for potential systems at ANL-E. The information derived from these contacts is summarized in Table 4. A common concern expressed by each company is that their estimates are only approximate and will depend on the off-gas system requirements. Additional discussions with each company are needed to determine which melter is best suited for this program.

Table 4. Summary of Vitrification System Availability

Company	Melter Type	Estimated Costs	Comments
GTS Duratek	Joule Heating	\$200K for 10 kg/day \$1000K for 100 kg/day [cost includes feed system, melter, off-gas system, installation]	GTS Duratek is installing a 300 kg/day unit at DOE-Fernald. This unit has run surrogate feeds and will start processing actual waste streams in November 1993. They have extensive experience with a variety of waste streams and off-gas systems.
StirMelter, Inc.	Joule Heating Stir Melter	\$125K for 100kg/day \$1125 for 500kg/day [cost includes feed system, melter, off-gas system, installation]	StirMelter's design allows vitrification to be performed at lower temperatures and more thoroughly homogenizes the melt. Lower temperatures may result in less challenging off-gas and volatility concerns.
Envitco	Joule Heating	\$450K for 300kg/day, melter unit only	Envitco is interested in establishing a demonstration unit at a DOE facility.

Economics of Vitrification

A vitrification system, including the melter, power source, feed systems, and off-gas systems suitable for treatment of ANL-E mixed wastes, will cost between \$225K and \$1200K, depending on the system selected. These costs are preliminary and need to be confirmed with each vendor to ensure that the prices quoted are for systems that include comparable components that meet ANL's technical specifications. These relatively large costs will be offset by savings realized as a result of volume reduction and low-level radioactive waste disposal costs. The economic benefits that can be expected from vitrification of ANL-E mixed wastes cannot be determined until the final waste streams and volumes are identified.

Volume Reduction

The volume reduction will strongly depend on the waste loading of the final product. For instance, if the evaporator bottom sludge is the only material treated, then some additives will be required to produce an acceptable glass. Volume reduction will result from the loss of water in the sludge and from the decomposition of the salts and subsequent release of compounds of SO_x , NO_x , and CO_2 . The volume reduction resulting from these processes is conservatively estimated at approximately 70%. This volume reduction would be offset to some unknown degree by the volume addition imposed by the glass-forming additives.

The most economic vitrification strategy is to take advantage of the chemistry of waste streams and blend them to minimize or eliminate additives. If the evaporator sludge bottoms are blended with the HEPA filter wastes, then the process realizes all of the volume reductions (approximately 70% for the sludge and approximately a factor of 100 for the HEPA filters) and less (possibly none) of the volume additions. A volume reduction of this magnitude could result in huge cost savings for the HEPA filter waste alone, where the waste disposal costs if the volume is not reduced are estimated at approximately \$700K vs. approximately \$50K for the volume-reduced HEPA filters. This waste minimization strategy is identical to the one currently being employed at Fernald, Ohio, in the MAWS program.

Disposal Costs

The disposal costs after vitrification will be reduced from \$150/ft³ for mixed waste to \$70/ft³ for low-level radioactive wastes. Note that the uncertainty of Hanford's willingness to continue to accept mixed wastes, coupled with the requirements of the Federal Facilities Compliance Act (FFCA), suggests that this cost savings may be conservative.

Summary

Five technical concerns expressed by WMO have been addressed in this report:

- (1) Can the mixed-waste streams be vitrified, resulting in a waste form that passes the TCLP test, and thus, is no longer considered a mixed waste?

Our preliminary study has demonstrated that surrogate mixed-waste streams can be vitrified. The nature and timing of this study have precluded the production of demonstration vitrification and TCLP testing with actual mixed waste. Facilities, personnel, and technical expertise are available to proceed with this demonstration upon receipt of appropriate direction and funding.

- (2) What are the realistic concentration levels of hazardous constituents that can be handled by a vitrification system?

Studies of silica glass chemistry indicate that mercury and silver are the hazardous metals whose solubilities may be limited. Based on our preliminary estimates of waste loadings in a potential ANL glass waste form, these limits would be approached when the concentration of these metals in the waste stream reached 3000 ppm. However, these limits may be avoided by lowering the waste loading in the glass.

- (3) Are there any indications that operation of a vitrification system would not be allowed by agencies such as the EPA, State of Illinois, etc.?

Initial correspondence with the Illinois EPA has indicated that a vitrification system would not be subject to the same regulations and scrutiny as an incineration unit. Instead, it will be considered a thermal treatment unit.

- (4) Can the expected off-gases be handled by off-the-shelf systems?

Compounds of SO_x , NO_x , and CO_x are significant off-gases expected to be generated during vitrification, with lesser amounts of Cl and F. These off-gases are commonly controlled with off-gas systems that are commercially available. The extent that each of these compounds must be controlled will be experimentally estimated during the laboratory crucible studies proposed for this project.

- (5) Are vitrification systems currently commercially available that can meet the anticipated technical specifications for the projected ANL-E system including capacity and off-gas systems?

Preliminary contacts with commercial vendors indicate that off-the-shelf units are available. Each vendor emphasized that, until we can provide specifics regarding the feed stream, they are unable to specify what components are needed to provide a system that meets ANL's technical specifications. This information will thus be obtained after the laboratory crucible studies.

Conclusions

This report indicates that using vitrification to treat some of the mixed wastes at ANL-E should be considered on the following bases:

- (1) There is a strong technical justification for using vitrification to treat mixed wastes and produce a final waste form that will be considered a low-level radioactive waste. There do not appear to be any technical limits to the hazardous metal concentration in the ANL-E mixed waste streams that can be handled.
- (2) Vitrification is a robust technology that can be used to treat existing, known mixed waste streams, as well as future mixed wastes that may need to be treated at ANL-E.
- (3) The potential cost savings associated with vitrification make this treatment method attractive. This savings arise primarily as a result of volume reduction and the conversion of mixed waste to low-level waste.
- (4) Commercial off-gas systems can be used to control off-gases to meet all safety and regulatory requirements.
- (5) Preliminary informal contacts with the State of Illinois and the EPA indicate that a vitrification facility at ANL-E would not be subject to the rigorous, intense scrutiny commonly associated with incineration facilities.
- (6) Vitrification systems are currently available from several commercial firms. Rough estimates of the cost of a facility suitable for ANL-E range from \$200K to \$1200K, depending on the facility size.

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Appendix A

Vitrification Processes (report reproduced from USEPA-1992)

CHAPTER THREE

TYPES OF VITRIFICATION PROCESSES

This report divides vitrification technologies into two categories: electric process heating and thermal process heating using fossil fuels. Electric processing can be subdivided into 3 primary groups: (1) joule heating, (2) plasma heating, and (3) microwave heating. Both joule heating and plasma heating are based on well-developed electric-furnace technologies for metal melting, metal smelting, and glass melting. Joule heating includes ex situ furnaces and ISV. In addition, several alternative electric heating processes of varying applicability to vitrification are described under Section 3.1.4, "Miscellaneous Electric Heating." All of these categories are described in greater detail in Maurice Orfeuil's Electric Process Heating. Much of the information in this chapter is summarized from Orfeuil's book (see also Pincus and Diken, 1976; Trier, 1976). The discussion of vitrification technologies in this chapter follows the outline presented in Table 3-1. Identified studies of the applicability of these processes to various wastes are presented in Appendix A.

During research for this document, several high-temperature, non-vitrification methods were discovered that immobilized waste in a crystalline rather than glass form. These included Ceramic Bonding, Inc. (Melzer, 1990)

Table 3 -1. Classification of Vitrification Processes

	Examples
1. Electric Process Heating	
A. Joule Heating	
(1) ex situ	Ceramic Melter
(2) in situ	In Situ Vitrication
B. Plasma Heating	Plasma Furnace
C. Microwave Heating	Microwave Melter
D. Miscellaneous Electric Heating	Resistance Heating, Induction Heating, Electric Arc Heating
2. Thermal Process Heating	Rotary Kiln Incinerator (operated in slagging mode)

and Molten Metals Technology, Inc. (Roy, 1991). While these technologies may be applicable to many of the same wastes as vitrification, it was felt that inclusion of these types of processes was beyond the scope of this document. Therefore, this document is limited to processes that use high-temperatures to produce a waste form that is all or largely glass.

3.1 Electric Process Heating

Many types of electric heating processes are potentially applicable to vitrification. Joule, plasma, microwave, induction, and electric arc heating are the electric processes currently being applied to vitrification.

3.1.1 Joule Heating

In joule heating, an electric current flows through the material. As the material internally resists the current, the current loses power and transfers heat energy to the material. The dissipated power is predicted by Joule's Law:

$$P = I^2R$$

where P = dissipated power (watts, W),
 I = current through the material (amperes, A), and
 R = resistance of the material (ohms, Ω).

Thus, with increased electrical resistance, if current can be maintained, additional power is dissipated and the material heats more rapidly. However, unless the voltage is increased, an increase in resistance will also decrease current. This is predicted by Ohm's Law:

$$R = V/I \text{ or } V = IR$$

where V = voltage (volts, V),
 I = current, and
 R = resistance.

Ohm's Law explains why materials with low resistivity are often heated at low voltages (5 to 48v) in non-vitrification

processes. However, soils and other materials heated by joule heating are frequently quite resistant and require higher voltages.

Several properties of glass impact the joule heating process. Among these properties is glass's poor electrical conductivity (high resistivity) as a solid. Conversely, at high temperatures, especially in the liquid state, glass is a more efficient electrical conductor and can be heated directly by electric current. Glass resistivity decreases by a factor of 10^{13} to 10^{14} as temperatures increase from ambient temperature to 1300-1400°C. This is explained by the structure of glass: current flow takes place due to the mobility of ions in the silica framework. As increased heating input breaks apart the framework, ions are increasingly able to carry the electric charge (Orfeuil, 1987). Figure 3-1 illustrates the decreased resistivity of selected glasses as temperature increases.

The resistivity and melting point temperature of a particular glass are also influenced by the chemical composition of that glass. Alkali content is particularly important in carrying charge. For equal alkali content, electrical conductivity is inversely proportional to the size of the ions. Therefore, sodium glasses have a higher electrical conductivity than do potassium glasses. However, conductivity is not related by a simple equation to the concentration or size of ions, and in general, only measurements can provide electrical resistivity values (Orfeuil, 1987).

Melt viscosity is the most important processing property; it controls processing rate, product homogeneity, and heat transfer within the molten glass. It exerts this control primarily by impacting convection currents (Orfeuil, 1987). Viscosity is modified by changing feed composition or process temperature.

Mechanical Constraints. Characteristics of the molten glass place mechanical constraints on the design of a joule heating system. For example, since the conductivity of molten glass is ionic, an alternating current (AC) must be used to avoid the risk of electrolysis, anodization of electrodes, and the depletion of charge carriers (Orfeuil, 1987).

Electrodes must withstand corrosion from the molten glass bath, offer adequate mechanical strength at high temperatures, and have low resistivity. The commercial glass industry generally uses graphite and molybdenum for electrodes.

The position of the electrodes in the furnace controls the buildup of convection currents in the melt and, subsequently, homogeneity in the melt. Their arrangement with respect to each other, and with respect to the top melt

level, controls the energy given off and enables the best possible glass melting conditions to be obtained. The concentration of energy around the electrodes causes local heating, resulting in an upward movement of the glass and convection currents in the bath.

Joule heating vitrification can be carried out both *ex situ* and *in situ*.

3.1.1.1 Ex Situ Joule Heating

Joule process heating furnaces for the treatment of hazardous wastes evolved directly from glass melters in the glass industry. The electric furnace/melter category includes processes that use a ceramic-lined, steel-shelled melter to contain the molten glass and waste materials to be melted.

Some melters are much like electric glass furnaces used to manufacture glass products (e.g., bottles, plates). Such melters receive waste materials and glass batch chemicals directly on the surface of a molten glass bath. Most melting occurs at the waste/molten glass interface as heat is transferred from the molten glass. As waste is heated, volatiles may be released and organics are either pyrolyzed (in an oxygen-poor environment), or oxidized (in an oxygen-rich environment). Off-gas treatment is required to minimize air emissions. Figure 3-2 shows a process flow-sheet for a typical joule-heated ceramic melter (JHCM).

Figure 3-1. Relationship Between Resistivity and Temperature for Selected Glasses (Orfeuil, 1987)

Figure 3-2. Typical JHCM Process Flowsheet (adapted from Koegler et al., 1989)

The molten glass melt has several distinctive characteristics which influence processing conditions and, ultimately, contaminant destruction and product formation. The more important of these will be briefly described here.

The melt is initiated by some form of pre-heating. Once the glass is fluid and conductive, heating continues by joule heating, as described earlier. Melt temperatures generally range from about 1000°-1600°C (Chapman, 1984). Maximum temperatures are limited to prevent corrosion of electrodes or refractory material and volatilization of constituents.

For many glass melters, an important part of the vitrification process is the formation of a cold cap, or crust on the top of the melt (Figure 3-3). The cold cap forms from the feed as it is introduced from the top of the melter and functions as the interface between the incoming material and the molten glass. Water evaporates from the top of the cap and enters the off-gas system. The cap's bottom contacts the glass and is the interface where feed material melts and forms the waste glass matrix. The cold cap performs the important function of filtering and holding volatilized wastes for possible re-incorporation into the melt.

Figure 3-3. Generalized JHCM Showing Components of Melter and Molten Material

In addition to the cold cap, other zones of non-glassy material may form in the melter. If the melt is strongly reducing, metals in their elemental form may sink and form a layer on the bottom of the melt. This electrically conductive layer may short the system and shut down the melter. Solutions for this difficulty include melter design, electrode placement, feed modification, and an additional tap on the bottom to remove metal slag separately from the glass. Metals which commonly form a slag include palladium, ruthenium, rhodium, silver, iron, and other heavy metals. This metal layer may potentially be recycled.

A salt layer may also form. Salt layers float on top of the melt and could cause shorting and corrosion (Eisenstatt and Chapman, 1986).

Electric furnace melting may result in several types of processing problems. Among these are:

1. Foaming (possibly caused by oxidizing conditions) may lead to unstable operations and pressure surges. Prolonged glass foaming may also lead to corrosion of refractory walls (Holton et al., 1988).
2. Cold-cap bridging (occurring when liquid flows under the cold cap) creates a high pressure zone which may result in uncontrolled glass discharge (Holton et al., 1988).
3. High electrical conductivity in the melt may cause the current required to heat the glass to exceed the recommended maximum current density for the melter electrodes.
4. Low electrical conductivity in the melt may result in a high voltage potential, causing conduction within the refractory material. Low conductivity also requires large electric power systems (Koegler et al., 1989).
5. High viscosity may slow the processing rate because the interaction rate between feed and glass is slowed (Koegler et al. 1989).
6. Low viscosity (<100 poise) may result in increased melter corrosion.

However, these problems are amenable to feed modification and other types of processing adjustments.

Other melters involve feeding mechanisms that introduce waste materials below the molten glass surface. Such methods of introduction result in the pyrolysis of organic contaminants within the molten glass, followed by evolution of pyrolyzed off-gases to the plenum (the space above the glass surface) where they may combust.

Undestroyed organics and organic by-products then move to the off-gas treatment system for removal. Both types of melters result in the incorporation of low-vapor-pressure inorganics into the molten glass.

Electric melters must periodically be tapped (drained) to remove the accumulated glass product. The molten glass may be cast directly into containers or sand. Another alternative uses a water bath (quench bath) to produce a granular residual product (aggregate).

Following is a description of several innovative melters that fall into the category of joule heated melters.

Stir-melters. Stir-melters are joule heated melters in which the molten material is agitated by a stirrer (Richards and Lacksonen, 1991; Bickford et al., 1991). Because this increases efficiency in heat distribution, stir-melters have a high throughput rate for their size. Throughput rates with the stirrer operating have been eight times greater than those without the stirrer operating. The greater efficiency in heat distribution also permits operation of the stir-melter at lower temperatures, thus allowing increased flexibility in selection of materials for melter components and increased contaminant incorporation into the waste glass. The increased throughput rate means the stir-melter can be constructed small enough to be used in gloveboxes for the treatment of radioactive materials. The smaller size and lower operating temperatures also reduce costs by reducing heat losses.

Liquid-fed Ceramic Melters (LFCM). The LFCM is currently the state-of-the-art melter for HLW. The advantage of the LFCM is that it is capable of converting high-level liquid wastes (HLLW) directly into glass without pre-calcination. Because it avoids calcination, the entire process is simplified and costs are substantially reduced. Seven projects are formally committed to the LFCM: Savannah River's Defense Waste Processing Facility (DWPF), USA; West Valley Demonstration Project, USA; Hanford Waste Vitrification Project, USA; Germany's PAMELA plant at Mol, Belgium; Wackersdorf, Germany; and Japan's Vitrification Facility (Chapman and McElroy, 1989).

3.1.1.2 In Situ Joule Heating

In situ joule heating is represented by ISV. ISV evolved from joule-heated glass melters developed to immobilize radioactive wastes. It was developed by Battelle at Pacific Northwest Laboratory (PNL) for the U.S. Department of Energy (DOE). The ISV process has been developed and demonstrated through large-scale testing. Wastes treated include a variety of hazardous chemical, radioactive, and mixed (hazardous chemical and radioactive) wastes.

ISV converts contaminated soil and other substrates into a stable glass and crystalline product. Figure 3-4 depicts the process. The Electrode Feed System (EFS) inserts a square array of four graphite electrodes into the contaminated site. This mechanism allows the electrodes to sink to increasingly greater depths as the molten glass increases in volume. Processing continues until the desired treatment level is reached, or until a process-limiting depth is reached. If processing difficulties are encountered, then EFS can "grasp" the electrodes and thus prevent their downward movement until the difficulty is addressed. Previously, ISV required insertion of the electrodes into boreholes prior to vitrification.

Because soil is not electrically conductive when moisture has been driven off, a conductive mixture of flaked graphite and glass frit is placed between the pairs of electrodes as a starter path. An electrical potential is applied to the electrodes to establish an electrical current in the starter path. The resultant power heats the starter path and surrounding soil to 2000°C, well above initial soil-melting temperatures of 1100°C to 1400°C. The graphite starter path is eventually consumed by oxidation and the current is transferred to the molten soil, which is electrically conductive when molten. As the molten or vitrified zone grows, it incorporates radionuclides and nonvolatile hazardous elements, such as heavy metals, into the melt and pyrolyzes organic components. The pyrolyzed by-products migrate to the surface of the vitri-

fied zone where they combust in the presence of oxygen. A hood placed over the vitrified area directs the gaseous effluents to an off-gas treatment system (Buelt, Timmerman, and Westsik, 1989).

Attempts to reduce costs by utilizing a fabric hood were not successful. Fabric hoods have caught fire twice in ISV tests, once during a PNL test and once during a Geosafe test. Both fires started when molten material splashed on the hoods. The hoods used at the time of the fires were fabric hoods coated with heat-resistant sealants. Since these fires, both PNL and Geosafe have reverted to previous steel hood designs. This change from fabric hoods to steel hoods has delayed the application of ISV to several sites.

As the melt grows downward and outward, power is maintained at sufficient levels to overcome heat losses from the surface and to the surrounding soil. Generally, the melt grows outward beyond the electrodes to a distance equal to about half of the spacing of the electrodes. For example, if the electrode spacing is 5.5 m, a melt width of about 8.5 m would normally be observed. The molten zone is roughly circular and somewhat flattened. The tendency to flatten increases as melt size increases (Buelt, Timmerman, and Westsik, 1989).

In order to control the amperage during ISV processing, operators use a power transformer with multiple voltage

Figure 3-4. Schematic of ISV (adapted from USEPA, 1989b)

taps. At start-up, the ISV process requires high voltage (up to 4,000 V) to overcome the resistance of the soil. Current is relatively low (400 A) at this time. As the melt progresses and resistance decreases, voltage is decreased (down to 400 V by the end of processing) to compensate for the decreased resistance of the molten glass and the resulting increase in current (up to 4,000 A by the end of processing). Processing continues until heat loss from the melt approaches energy delivered to the soil via the electrodes, or until power to the electrodes is shut off (Jacobs et al., 1988).

Five major subsystems comprise the process equipment to perform ISV: (1) electrical power supply, (2) off-gas hood, (3) off-gas treatment, (4) off-gas support, and (5) process control (Buelt, Timmerman, and Westsik, 1989). These five major subsystems and their set-up at a typical site are depicted in Figure 3-5. Except for the off-gas hood, all components are contained in three transportable trailers. The off-gas hood and off-gas line, which are installed on the site for collecting gaseous effluents, are dismantled and placed on a flatbed trailer for transport between the sites to be treated.

The normal processing rate for the large-scale system is 3 to 5 tons/hour (t/h). The maximum depth demonstrated thus far has been 5 m (17 ft) by PNL and 5.8 m (19 ft) by Geosafe. The average processing operation lasts about 150 to 200 hrs, depending upon the depth and electrode spacing (Buelt, Timmerman, and Westsik, 1989).

ISV processing is termed "in situ" when the soils are processed where they presently exist. Placing soil in a trench or container for treatment is termed "staged"

processing. For example, a staged application may involve consolidating contaminated soil by removing the soil and placing it in a trench. The filled trench could then be vitrified. Typically, staged application would be most effective where the contaminants are widely distributed in the top few feet of the site. Because ISV is a batch process, it may not be cost effective to move the hood from setting to setting to vitrify the top few feet of the contaminated material.

A predictive model of the ISV process has been developed at PNL to assist engineers and researchers in the application of ISV to different sites. The model, configured on a Macintosh personal computer, predicts vitrification time, melt depth and width, and electrical consumption. Predictions are based on data inputs of electrode configuration, soil parameters, and molten-glass characteristics. The model's predictions are useful for operations planning, cost estimates, and melt locations. The depth and width predictions, for example, can be used to locate the melts to help ensure that the entire contaminated region is treated and that adjacent structures are not damaged by ISV treatment. Using the model to predict the shape of a large-scale ISV melt indicated close agreement between model prediction and actual monolith shape. Further validation testing is needed, however (Koeqler and Kindle, 1991).

3.1.2 Plasma Heating

Plasma heating is an electrical heating process which relies on the conversion of a gas into a plasma through the application of energy by an electric arc. Plasma heating offers high operating temperatures and high power densi-

Figure 3-5. Pilot-Scale Process ISV (adapted from Callow, Weldner, and Thompson, 1991)

ties. Unlike joule heating vitrification, which grew out of the glass-making industry, plasma heating vitrification has grown out of the specialty metals industry.

A plasma is an ionized gas. At high enough temperatures (e.g., 20,000°K for argon), electrons are stripped from their nuclei and the matter exists as a mixture of negative electrons, positive nuclei, and atoms. The ionized particles make plasma an excellent electrical conductor (Jacob 1991; Orfeuil, 1987).

There are two types of plasmas: plasmas in which the degree of ionization is close to unity and plasmas which are only partially ionized (Jacob, 1991). The first type of plasma occurs in thermonuclear fusion, in which temperatures reach several millions of degrees. This is the type of plasma found in the sun and which has no industrial application at present. In partially ionized plasmas, the degree of ionization varies from 2 to 50%. The temperatures of partially ionized plasmas vary between 2,000°K and 5,000°K. It is these plasmas that have industrial application (Jacob, 1991; Orfeuil, 1987).

Plasma heating equipment must perform two basic functions: creating the plasma and effectively heating the product.

Plasma is commonly created by passing a gas through an electrical arc. The arc can be generated by direct current (DC) or alternating current (AC). With a DC arc the cathode generally consists of tungsten and the anode generally consists of copper. The anode also typically functions as a nozzle directing the plasma. In contrast, in a single phase AC arc plasma generator, the electrodes act as the cathode and anode alternately, and must therefore be made from the same material.

Gases used in generating a plasma arc include nitrogen, oxygen, noble gases, air, and mixtures of these gases. Electrode life is a major concern and is influenced by electrode material, the gas used, and electrical current levels. Electrode structure, gas injection method, and nozzle design help shape the plasma and determine heating efficiencies.

The product is heated in one of two ways: by a non-transferred arc or by a transferred arc (see Figure 3-6). A non-transferred arc uses two internal electrodes. A small column of injected gas is heated by the electric arc, creating a plasma flow that extends beyond the tip. Non-transferred arcs heat only via conduction and produce a dispersed heat that is needed for tasks such as air and gas heating and drying. Non-transferred arcs have been applied to hospital wastes.

A transferred arc uses the working material as one of the electrodes. Therefore, in a transferred arc application, heating occurs via convection, radiation, and electrical resistance. It is the transferred arc that is the heat source in hazardous and radioactive vitrification applications. In these applications, the plasma arc melts the material to form a molten bath from which glass is periodically removed to form the immobilized waste product.

The application of plasma heating to hazardous material is international in scope. Kupf, a German firm that was recently purchased by Mammesman Demag, has developed an AC transferred arc torch with a tungsten tip that has application to hazardous materials. Aerospatiale, a French company, has a non-transferred arc torch with application to medical wastes. Tetronics Research and Development Company in Faringdon, England, has researched treatment of contaminated soil and incinerator ash. Davy McKee's Research and Development Group in Stockton-on-Tees, England, is working on a plasma furnace for treating arc furnace dusts by recovering the metals and leaving a material suitable for landfill (Jacob, 1991).

In the United States, Plasma Energy Corporation (PEC) has a transferred arc plasma torch that has been used in industrial applications in the past and is now being applied to the vitrification of ash from the incineration of municipal solid waste (MSW) in Japan. In one effort, Ebara and

Figure 3-6. Comparison of a Transferred Arc and a Non-Transferred Arc (Source: Plasma Energy Corporation)

Infilco are applying the PEC torch at a pilot-level plant. In the United States, PEAT, Inc. is researching the application of the PEC torch to medical wastes and incinerator ash.

Retech, Inc. of Ukiah, California has developed a plasma heating furnace called the plasma centrifugal reactor (PCR). In the PCR, prepared waste materials are fed into a rotating reactor in which a transferred-arc plasma torch is operating. The rotating reactor also serves as one electrode for the transferred arc. The plasma torch, which is capable of temperatures exceeding $10,000^{\circ}\text{C}$, heats the waste material beyond the point of melting to about $1,600^{\circ}\text{C}$. Centrifugal force created by the rotating reactor prevents waste and molten material from flowing out of the reactor through the bottom. The rotation of the reactor also helps to transfer heat and electrical energy evenly throughout the molten phase. Periodically, the melted material is allowed to fall into a slag chamber where it is collected in waste containers (Eschenbach, Hill, and Sears, 1989). Figure 3-7 is a schematic of a demonstration PCR; it shows the location of the electrodes and the way in which the molten glass pools due to centrifugal forces.

Organics and other volatiles emitted during the plasma heating pass from the reactor chamber to a secondary combustion chamber into which an oxidizing gas is added, thus allowing for further destruction of any organics remaining in the gas phase. Resulting off-gases are then transferred to an off-gas treatment system to ensure safe air emissions.

Figure 3-8 illustrates the components of a full-scale PCR, including the feed system, reactor, secondary combustion chamber, slag chamber, and off-gas system.

3.1.3 Microwave Heating

In microwave heating, a form of dielectric heating, the body to be heated absorbs electromagnetic radiation. More specifically, a dielectric is a material which is an electrical insulator. A dielectric becomes polarized when it is placed in an electric field. If the electric field is alternating, successive distortion of the molecules causes heating (Orfeuil, 1987). Ceramic-like wastes such as incinerator ash, thermal insulators, concrete, soil, and sand are mostly composed of dielectric material and can

Figure 3-7. Schematic of the Demonstration PCR Showing the Bottom-Pour Configuration for Exit Gas and Molten Glass (Eschenbach, Hill, and Sears, 1989)

Figure 3-8. Schematic of a Full-Scale PCR (Eschenbach, Hill, and Sears, 1989)

be directly melted by microwave radiation (Komatsu et al., 1990).

Dielectric heating is usually classified into two sub-categories on the basis of frequency ranges used: radio frequency heating using frequencies between 10 and 300 MHz, and microwave heating using frequencies between 3,000 and 30,000 MHz (Orfeuil, 1987). Of these two forms of dielectric heating, only microwave heating has been used to vitrify hazardous wastes.

A microwave installation consists of a microwave generator, a waveguide, an applicator, and ancillary monitoring, handling, and safety devices (Fig. 3-9). The microwave generator produces the microwaves that dielectrically heat the load material. The waveguide directs the microwaves from the generator to the load material by reflecting the microwaves from its metal walls; it also keeps radiowaves from propagating in all directions. Applicators define the way in which the microwaves are applied to the load material. There are many types of microwave applicators. These applicators vary depending on the type of process, continuous or batch, and the nature and shape of the load material (Orfeuil, 1987). Ancillary monitoring, handling, and safety devices work much as those used in other types of treatment processes.

The main advantage of microwave heating is that the heat is produced directly and solely in the mass of the material to be heated. Another advantage is high power density.

The main disadvantage is relatively high energy consumption and corresponding costs (Orfeuil, 1987). Arcing resulting from induced currents in metallic components of waste may damage the microwave generator unless special provisions are made.

Kobe Steel, Ltd. has developed an incinerator/microwave melter treatment process for plutonium contaminated solid waste at the Plutonium Waste Treatment Facility (P WTF) in the Tokai Works of the Power Reactor and Nuclear Fuel Development Corporation (PNC) (Miyata et al., 1989, Ohuchi et al., 1989). In this process, plutonium contaminated solid waste is incinerated and the ash is passed to the microwave melter. The microwave system consists of a melter, ash feeding system, microwave

Figure 3-9. Microwave Melter (Orfeuil, 1987)

feeding system, and the waveguide are all contained within a glove box for safety in handling the radioactive material. Only the microwave generator is outside the glove box. Generated microwaves are introduced into the glove box via the waveguide. The microwave melter operates in batch feed. In this process, the material to be treated is placed in crucibles before vitrification. These crucibles serve as melt containers and, ultimately, storage containers for the waste glass.

The microwave melter has also been demonstrated on slurry produced from a nuclear reactor. Melting and immobilization occurred in crucibles that were later capped and then welded by a remote-controlled plasma arc welder (Komatsu et al., 1990).

Kobe Steel is now seeking to apply microwave heating to a wide variety of non-combustible wastes, including liquid and sludge wastes, inorganic insulators (such as asbestos and rock wool), residues of acid digestion and direct liquid wastes, concrete, contaminated soil and sand, and radioactive contaminated wastes.

In America, the DOE is researching the application of microwave vitrification to radioactive wastes. Bench- and pilot-scale tests have been conducted using actual transuranic (TRU) waste from Rocky Flats Plant. Results were similar to those from cold bench-scale tests and encouraged further research (Petersen, 1990). Methodology similar to the Japanese microwave methodology is also being developed at Oak Ridge National Laboratory (ORNL).

3.1.4 Miscellaneous Electrical Processes

Several electrical heating methods have been used in vitrification, but not extensively. These include resistance heating, induction heating, and electric arc heating. Of these, electric arc heating probably represents the greatest potential for broad application to the treatment of hazardous waste, but it is still in the early stages of such development.

3.1.4.1 Resistance Heating

Initial large-scale testing of vitrification for HLW was done in crucibles heated by external resistance heaters. Their design represented a direct increase in scale from glass development crucible tests. Crucible heating was discarded as a treatment option for HLW because of low melt rates caused by slow heat transfer and lack of agitation and because temperature non-uniformities made it difficult to homogenize the glass (Bickford, Hrma, and Bowan, 1990).

3.1.4.2 Induction Heating

Currently, induction heating application to hazardous and radioactive wastes is represented by the French AVM process (Atelier de Vitrification Marcoule) and its descendants. However, because induction heating is also used in commercial glass manufacturing, it is potentially applicable to hazardous and radioactive wastes and will be briefly described here.

Induction heating is accomplished by inducing currents in the material to be heated. For example, a solenoid can be used to create a variable magnetic field inside the coil and around it. If an electrically conductive body is placed inside the magnetic field, the variation in the magnetic field causes a variation in the magnetic flux passing through the material and induces an electromotive force (EMF) current. The EMF current causes eddy currents, and these are converted into heat due to the Joule effect. Induction heating can also be created using highly varied induction configurations (flat inductors, linear inductors, tunnel inductors, etc.) and a wide range of relative part/inductors (Orfeuil, 1987).

The French have developed an induction-heating vitrification process preceded by calcination for their processing of HLW (Jouan, Ladirat, and Moncouyoux, 1986; Bonniaud et al., 1986; Baehr, 1989). This system, the AVM, has been operating since 1978 and is located at Marcoule, France. As of October, 1988 the AVM had vitrified 1,225 m³ of concentrated fission product solutions. These operations generated 540 tons of glass packaged in 1,547 metallic canisters (Baehr, 1989).

The AVM facility treats HLW in two primary steps: calcination and glass formation. The calcination process occurs first and drives off water, converts hydroxides to oxides, and sinters the material, thereby reducing surface area. The resulting calcine is mixed with appropriate glass-forming materials and melted in the induction-heated glass furnace.

Vitrification processes in several other locations are modeled on the AVM facility. In France, two new, sister vitrification plants are being built at La Hague. The English are employing a similar system to vitrify English HLW at Sellafield (*Nuclear Engineering International*, 1990).

3.1.4.3 Electric Arc Furnaces

Electric arc furnaces also are being applied to vitrification; they heat by creating current flow between two electrodes in an ionized gas environment. They differ from plasma furnaces in that a plasma is not created and therefore not

part of the heat transfer mechanism. The electric arc furnace was first developed in the metal industry.

A group from Electro-Pyrolysis, Inc. is working with a group from Massachusetts Institute of Technology to develop an innovative vitrification process. In this process, a DC electric arc is used in connection with a plasma heating arc to pyrolyze solid hazardous materials. The electric arc provides the primary energy for the heating and melting of the target material. This occurs in a sealed unit, thus reducing overall the amount of gases produced during pyrolysis and allowing the gas to be removed from the system in a non-oxidizing atmosphere. Furthermore, because the chamber is sealed, generated gases are forced to exit upward through the hollow arc-generating electrode and must pass through the electric arc. In addition, a plasma-heated zone created by electron-beam ionization and microwave heating is located at the tip of the electrode; gases must also pass through this. Thus, the plasma functions as a scrubber for off-gases generated by the electric arc. The electric arc provides target material heating and also off-gas treatment (Bromberg et al., 1991).

An electric arc is also being used in the vitrification tests in Albany, Oregon of MSW bottom ash and fly ash and the ash from sludge incineration. These tests are in the shakedown stage in preparation for round-the-clock testing. The Bureau of Mines and the American Society of Mechanical Engineers are the primary sponsors of these tests. The Japanese are also working on electric-arc vitrification.

3.2 Thermal Process Heating

Thermal process heating differs from electric process heating in that the heat for melting is produced by the burning of the waste and/or fuel. The melting most commonly occurs in a rotary kiln operated in a slagging mode to produce a glass product, but other incinerators are also used to vitrify wastes. Fossil-fuel-fired glass furnaces have been used in the glass industry and may also be applicable to waste vitrification. This section describes several rotary kiln processes and one other thermal process used to vitrify wastes.

Rotary Kiln Incineration. A rotary kiln is a cylindrical, refractory-lined shell mounted at an incline from a horizontal plane. This cylinder is rotated to facilitate mixing of wastes under incineration with combustion air, as well as to promote transfer of wastes through the reactor. Constant rotation of the kiln also provides continuous exposure of fresh surfaces to oxidation to promote destruction. A rotary kiln system includes the waste feed system,

rotary kiln incinerator, auxiliary fuel feed system, after-burner, and air pollution control systems.

Wastes and auxiliary fuel are injected into the high end of the kiln and pass through the combustion zone as the kiln slowly rotates. Retention time can vary from several minutes to an hour or more. Wastes are substantially oxidized to gases and inert ash within this zone. Ash is removed at the lower end of the kiln, while flue gases pass through a secondary combustion chamber and then through air pollution control units for particulate and acid gas removal. Residual streams generated during rotary kiln incineration include bottom ash, fly ash, and scrubber wastewater (Johnson and Cosmos, 1989; USEPA, 1988).

Rotary kiln incinerators operated in the slagging mode may produce a vitrified product. At high enough temperatures, the material in the kiln will deform, producing an amorphous state in that material. This molten slag can then be tapped and may harden into a glass or glass-like product upon cooling, based on material composition (Brunner, 1984). Leachability tests were conducted on the hardened slag produced in a 50,000 metric tons/year rotary kiln operating at Rijnmond, Holland. Results indicated that the slag, as produced, would pass the EPA Toxicity Characteristics Leaching Procedure (TCLP) tests (Schlegel, 1989).

Kiln incineration may be used as a vitrification process by itself or prior to a vitrification step in a treatment train. Inorganic Recycling, Inc. (IRI) has developed a vitrification process using only incineration, while Marine Shale Processors (MSP) has developed a vitrification process in which only a portion of the incineration products are vitrified. These processes are described below.

IRI's kiln-driven process uses F006 waste (wastewater treatment sludges from electroplating) as feedstock to produce ceramic products. Metals in the waste feed increase the hardness of the glass-like products and also affect their color (*The Hazardous Waste Consultant*, 1990a). Figure 3-10 shows a flow diagram of IRI's recycling process. The process involves two primary operations: mixing and vitrification.

The mixing system operates in a batch mode. Before being mixed, each batch of F006 feedstock is tested to determine the amounts of other raw materials that must be added to the batch. In the mixing vessel, water and various chemicals are added to the waste and a series of oxidation-reduction reactions take place. After the reactions are complete, silicates, such as sand and clay, are blended with the feed. The mixture is then pumped into an agitated holding tank.

Figure 3-10. Flow Diagram of the IRI Process (adapted from *The Hazardous Waste Consultant*, 1990a)

The vitrification system operates continuously. Material is pumped from the holding tank into the kiln at a controlled rate. Kiln temperature is varied based on the composition of the feed. A pool of molten material forms in the kiln and rises to an overflow level. When it reaches the overflow level, the molten material flows out of the kiln and into the exit system.

According to IRI, the material produced in the recycling process has numerous potential uses. These include: architectural products, such as wall and floor tiles, patio stones, mosaics, sinks, tubs, and countertops; abrasive products, such as sandpaper, shot blast, and grinding media; and refractory products, such as high-temperature bricks and other insulating materials (*The Hazardous Waste Consultant*, 1990a).

In the MSP incineration/vitrification process, the hazardous materials may form the raw ingredients for an aggregate material. The primary elements of the processing

system are a 275-foot, counter-current rotary kiln where incineration occurs, a puddling furnace where vitrification occurs, and an off-gas treatment system where off-gases are treated (see Figure 3-11).

Sludges and solids are prepared for processing by blending. Included in this blend are the shredded containers in which the waste was stored or transported. The production of feed material by blending is controlled to produce a feed with a heat content between 18,600 and 25,570 joules/gram (8,000-11,000 BTU/lb). Raw ingredients are fed into the elevated end of the kiln and move toward the lower end with a residence time of 120 to 150 minutes. The lower end of the kiln is fired with natural gas and liquid fuels. Oxygen and air are also introduced at the lower end to support oxidation and maintain temperatures at approximately 1200°C. Solids exiting the lower end of the kiln are separated by size. Fine materials are sent to the puddling furnace to be vitrified, while large materials, such as gravels and ferrous materials, are stored for testing.

coal, and glass-forming ingredients enter the preheater from the top. The batch rapidly preheats in suspension by radiative and convective heat transfer. The preheater is designed to burn pulverized coal or a variety of gaseous, liquid, and coal-slurry fuels. The preheated batch ingredients are separated against the walls of the cyclone melter by centrifugal forces. The liquid phase reactions occur along the walls, and the melted glass and combustion gases exit the melter to the melt reservoir. The melt reservoir gives material more time to form a glass, and is designed to hold an adequate supply of glass for level control or temperature conditioning. The melted glass may then be delivered to a glass forming process, or other glass conditioning device, for integration with a glass manufacturing process. The combustion gases exit the melt reservoir to a high-temperature recuperator where waste heat is recovered and recycled to the preheater. Off-gas contaminants may also be recycled to the preheater to increase process destruction efficiencies (DE's).

The primary source of energy for melting process residue in the puddling furnace is the gases from the incineration process. This is augmented with a natural gas/oxygen lance that fires upon the molten surface. Puddling furnace by-products are fed to the smelting section while the lava migrates to the lower section of the smelter and enters a pooling pot (Harlow et al., 1989).

Multi-fuel Glass Melter. Vortec has developed a multi-fuel glass melter with application to hazardous wastes (Hnat et al., 1990b). The Cyclone Melting System (CMS) is composed of three primary components: a multi-fuel-capable batch preheater, a cyclone melter, and a glass melter reservoir. Preheated combustion air, pulverised

Figure 3-11. Simplified System Schematic of MSP's Process (adapted from Harlow et al., 1989)

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