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Vitrification Technologies for Treatment of Hazardous and Radioactive Waste

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Vitrification Technologies for Treatment of Hazardous and Radioactive Waste

U.S. Environmental Protection Agency
Office of Research and Development
Center for Environmental Research Information
Cincinnati, OH 45268

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ACRONYMS

AC	Alternating Current
AEDC	Arnold Engineering Development Center
ANS	American Nuclear Society
ASTM	American Society for Testing Materials
AVM	Atelier de Vitrification Marcoule
BDAT	Best Demonstrated Available Technology
CERCLA	Comprehensive Environmental Reponse, Compensation, and Liability Law
CMS	Cyclone Melting System
DC	Direct Current
DE	Destruction Efficiency
DNT	Dinitrotoluene
DOD	Department of Defense
DOE	Department of Energy
DRE	Destruction and Removal Efficiency
DWPF	Defense Waste Processing Facility
EDTA	Ethylenediaminetetraacetate
EMF	Electromotive Force
EFS	Electrode Feed System
EP Tox	Extraction Procedure Toxicity
EPA	Environmental Protection Agency
GRI	Gas Research Institute
HEPA	High-Efficiency Particulate Air
HLLW	High-Level Liquid Wastes
HLW	High-Level Waste
IAEC	International Atomic Energy Commission
INEL	Idaho National Engineering Laboratory
IRI	Inorganic Recycling, Inc.
ISV	In Situ Vitrification
JHCM	Joule Heated Ceramic Melter
LFCM	Liquid Fed Ceramic Melter
LX	Leachability Index
MCC	Materials Characterization Center
MIIT	Materials Interface Interactions Tests
MSP	Marine Shale Processes
MSW	Municipal Solid Waste
NBS	National Bureau of Standards
NEPA	National Environmental Policy Act
ORNL	Oak Ridge National Laboratory
OSHA	Occupational Safety and Health Administration
OSWER	Office of Solid Waste and Emergency Response
PCB	Polychlorinated Biphenyl

ACRONYMS (continued)

PCR	Plasma Centrifuge Reactor
PCT	Product Consistency Test
PEC	Plasma Energy Corporation
PNC	Power Reactor and Nuclear Fuel Development Corporation
PNL	Pacific Northwest Laboratory
RCRA	Resources Conservation and Recovery Act
ROW	Recomp of Washington
RWMC	Radioactive Waste Management Complex
SITE	Superfund Innovative Technology Evaluation
SRL	Savannah River Laboratory
SRS	Savannah River Site
TCLP	Toxicity Characteristic Leaching Procedure
TNT	Trinitrotoluene
TRU	Transuranic
USATHMA	United States Army Toxic and Hazardous Materials Agency
USEPA	United States Environmental Protection Agency
UST	Underground Storage Tanks
V/S	Volume of leaching solution/Surface area of solids
VOC	Volatile Organic Compound
WIPP	Waste Isolation Pilot Plant
ZHE	Zero Headspace Extractor

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CHAPTER ONE

INTRODUCTION

1.1 Purpose

Vitrification, the process of converting materials into a glass or glass-like substance, is increasingly being considered for treating various wastes. Vitrification is conceptually attractive because of the potential durability of the product and the flexibility of the process in treating a wide variety of waste streams and contaminants. These characteristics make vitrification the focal point of treatment systems for high-level radioactive waste (HLW) around the world.

This handbook presents the theory behind the vitrification process and overviews the applications and limitations of vitrification for waste treatment. Accordingly, it classifies the types of vitrification processes which have been applied to waste treatment, explains why vitrification may be considered as a treatment process, identifies waste streams and contaminants to which vitrification may be applied, and discusses other issues important to the application of vitrification to waste treatment.

In overviewing vitrification in this way, this handbook relies primarily on publicly available information and reports. Rather than attempting to evaluate the quality of such information, this document simply presents the conclusions as stated in the reports. Wherever possible, it avoids unpublished vendor information and personal communications; however, it includes some vendor information in order to provide information and direction not publicly available. Even so, it does not use vendor information as the sole source to make new, unique, or unsupported claims about vitrification processes.

Vitrification may proceed in situ (in situ vitrification or ISV) or ex situ. ISV and ex situ vitrification have opposing strengths and weaknesses. An advantage of ISV is that it proceeds in situ without requiring that the material be removed prior to treatment. With very hazardous contaminants, such as radionuclides or dispersible volatile compounds, this may be a significant advantage. Furthermore, the product remains buried under ground and on-site, thus limiting liability by keeping the waste product on-site. Ex situ vitrification, on the other hand, does require excavation, or at least increased materials handling prior to vitrification, but is not limited to waste in the immediate area of electrode placement.

The advantages of ex situ over in situ lie primarily in the increased amount of control that can be exerted during processing. This control extends to feed composition and melt conditions and this in turn allows for greater control of product characteristics. For processes aimed at a specific waste stream, control is increased because of the relative homogeneity of the waste stream. Secondly, ex situ vitrification allows greater control over the combustion of non-pyrolyzed organics escaping from the melt. For these processes, the environments in the molten glass melt and in the secondary combustion area can be more easily regulated to facilitate efficient organic destruction. However, ISV does operate at higher temperatures (typically 1600-2000°C) than ex situ processes (typically 1000-1600°C) and thus may sometimes avoid the need for fluxants.

1.2 Overview

Glass is a rigid, noncrystalline material of relatively low porosity. It is often composed of constituents such as oxides of silicon, boron, aluminum, and alkali and alkaline earth elements. While phosphate, sulfide, and oxynitride glasses are also important glass types, most glasses used in waste immobilization are borosilicate, sodium silicate, or aluminosilicate glasses and this handbook limits its review to these glasses.

Vitrification is the process of converting materials into a glass or glassy substance, typically through a thermal process. Although heat is not necessarily required for vitrification (for example, vapor deposition, solution hydrolysis, and gel formation can also form glassy materials), this document considers only vitrification processes which use heat.

When accomplished through a thermal process, vitrification may destroy organic contaminants via pyrolysis or combustion. As a stabilization process, vitrification may immobilize inorganics by incorporating them into the glass structure or by encapsulating them in the product glass. Glass's ability to incorporate metals has a long history: selenium is found in clear glass bottles; chromium gives green glass its color; and lead oxide, at levels up to 30%, is found in lead crystal glass (McLellan and Shand, 1984).

Many contaminated materials contain adequate quantities of the raw ingredients needed for forming glass. When such materials are heated, the ingredients melt together and actually form the glass in which the contaminants are immobilized. Because not all contaminated materials do contain proper ratios of the materials for the formation of a glass, additives may be required for some materials to address these deficiencies. Additives may also be needed to create the special characteristics of some glasses.

Vitrification has four major advantages over other methods of waste management. The primary advantage is the durable waste glass it produces. In most instances, this waste glass performs exceptionally well in leach tests. Because of its chemical and physical durability, the vitrification product has been considered for recycling as aggregate and other products. The second major advantage of vitrification is the flexibility of the waste glass in incorporating a wide variety of contaminants and accompanying feed material in its structure without a significant decrease in quality. The third advantage is that vitrification processes can accommodate both organic and inorganic contaminants of various amounts. Lastly, vitrification may reduce the volume of waste material.

Vitrification's major limitation is that it is energy intensive and, thus, may be more expensive compared to other remedial technologies. A second major limitation is the potential for some contaminants, both organic and inorganic, to volatilize. This limitation applies to both ex situ processes and ISV. For ISV, there is some concern that certain contaminants may migrate into the surrounding soil. These limitations may be amenable to modification of process parameters given site characteristics and management goals.

Given these advantages and limitations, vitrification's niches may include waste with great potential hazard, waste which is highly concentrated, waste with a complex mix of contaminants, specialized industrial waste streams, and wastes where a high quality product is required. For example, vitrification is the treatment of choice for high-level waste (HLW) and is well worth the associated costs in treating this waste. In fact, EPA has declared vitrification to be a Best Demonstrated Available Technology (BDAT) for HLW (40 CFR 268.42, Table 3). Site conditions that may make any vitrification process attractive are low unit costs for electricity. ISV may be attractive at sites where concerns about company liability from off-site disposal drive treatment objectives.

1.3 Handbook Organization

Chapter One, "Introduction," (the present chapter) identifies the purpose of this handbook, defines vitrification as it is used in this handbook, overviews vitrification applications, and summarizes handbook organization.

Chapter Two, "Glass Structure and Its Relationship to Vitrification," describes the structure of glass and relates this structure to the vitrified product. Because of its amorphous, non-crystalline structure, glass can immobilize a wide variety of inorganic contaminants, either by chemical incorporation into the actual glass matrix or physical encapsulation. Leaching of immobilized inorganics occurs via matrix dissolution and interdiffusion.

Chapter Three, "Types of Vitrification Processes," classifies vitrification into two major categories: electric process heating and thermal process heating. Electric process heating is the more important vitrification category and includes joule heating processes, both ex situ and in situ, plasma heating processes, microwave heating processes, as well as several miscellaneous heating processes. Thermal process heating is dominated by processes using rotary kiln incinerators, but other thermal processes may also be applicable to waste vitrification.

Chapter Four, "Applicable Waste Types and Contaminants," discusses waste streams and contaminants to which vitrification may be applicable. Waste streams discussed include radioactive wastes and sludges, contaminated soils, contaminated sediments, incinerator ashes, industrial wastes and sludges, medical wastes, underground storage tanks (USTs), drummed wastes, shipboard wastes, and asbestos wastes. Contaminants discussed include inorganics (metals, radioactive wastes, asbestos, and others) and organics. This chapter is meant to give the reader an understanding of vitrification's potential; it is not necessarily comprehensive or limiting in its scope.

Chapter Five, "Product Characteristics," addresses various components of product quality, volume reductions achieved with vitrification, and potential uses of the product glass. Generally, the vitrified waste is a high quality product. Waste glasses have performed well in a variety of leach tests, thus indicating high chemical durability. They have also shown high physical integrity and generally perform well even when devitrified, or re-crystallized. Furthermore, estimates indicate that waste glasses may exhibit these properties over geologic time spans.

Chapter Six, "Off-Gas Treatment," discusses off-gas concerns by describing typical off-gas components, off-gas constituents of concern, and potential means of off-gas control. Off-gas control may be approached in two ways: reducing emissions and treating evolved off-gases. Reducing emissions is accomplished through control of various process parameters. Methods for treating evolved off-gases are similar to those for other waste treatment processes.

Chapter Seven, "Capabilities and Limitations," summarizes the capabilities and limitations of vitrification.

Chapter Eight, "Physical and Chemical Testing," describes the physical and chemical tests used to determine the properties of targeted waste streams and of waste glasses. Described tests include, but are not limited to, the leach tests so important in determining waste form quality.

Chapter Nine, "Process Evaluation," addresses various issues which may be important in selecting a vitrification technology. Presented in this chapter are examples of technology screening studies, initial testing and scaling-up concerns, and a discussion of cost components. The discussion of cost components emphasizes cost categories and their relative importance to total clean-up costs.

CHAPTER TWO

GLASS STRUCTURE AND ITS RELATIONSHIP TO VITRIFICATION

Vitrification is attractive as a waste treatment process primarily because of the properties of glass. These properties give vitrification its high-quality product and flexibility in inorganic incorporation. Because an understanding of the properties of glass is fundamental to understanding the advantages of vitrification as a waste treatment process, this chapter offers a brief overview of glass structure and discusses how this structure relates to the durability of vitrified glass containing hazardous waste. This chapter is summarized mainly from McLellan and Shand (1984). Sections 2.3.3 and 2.3.4 are summarized from Wicks (1985, 1986). Because this chapter deals with the incorporation of inorganic contaminants into the glass structure, organic contaminants will not be addressed here.

2.1 Glass Structure

Glass is a rigid, noncrystalline material of relatively low porosity, often composed primarily of silica, alumina, and oxides of alkali and alkaline earth elements. While phosphate, sulfide, and oxynitride glasses are also important glass types, most glasses used in waste immobilization are silicate glasses. Therefore, this handbook limits its review to silicate glasses.

Thermally-formed glasses are produced by fusing or melting crystalline materials and/or amorphous materials (e.g., previously formed glasses) at elevated temperatures to produce liquids. These liquids are subsequently cooled to a rigid condition without crystallization. Most thermally-formed waste glasses, however, also have a crystalline phase. For example, while the ISV product is substantially glassy, it is actually a mixture of glass and microcrystalline phases. Glass composition is largely inorganic, with silica (SiO_2) being the most common constituent. From an engineering standpoint, what distinguishes glass from crystalline substances is the lack of a definite melting point temperature. When glass is heated, it will gradually deform and, at high enough temperatures, form a viscous liquid.

Silicate glasses are not composed of discrete molecules, but are three-dimensional networks. The basic structural unit of the silicate network is the silicon-oxygen tetrahedron in which a silicon atom is bonded to four oxygen atoms (Figure 2-1). The silica tetrahedra are linked at the corners, where each shares one oxygen atom with another tetrahedron (Figure 2-2). Some, or all four, of the oxygen atoms from the tetrahedron can be shared with other tetrahedra to form a three-dimensional network. What prevents these tetrahedra from forming a crystalline network is that the extended 3-dimensional network is irregular and the Si-O-Si bonds random (McLellan and Shand, 1984).

The shared oxygen atoms are called bridging oxygens. In pure silica glass, the ratio of silicon to oxygen is ideally 1:2 and all oxygen atoms are bridging. Some atoms, such as sodium, are ionically bonded to oxygen when present in

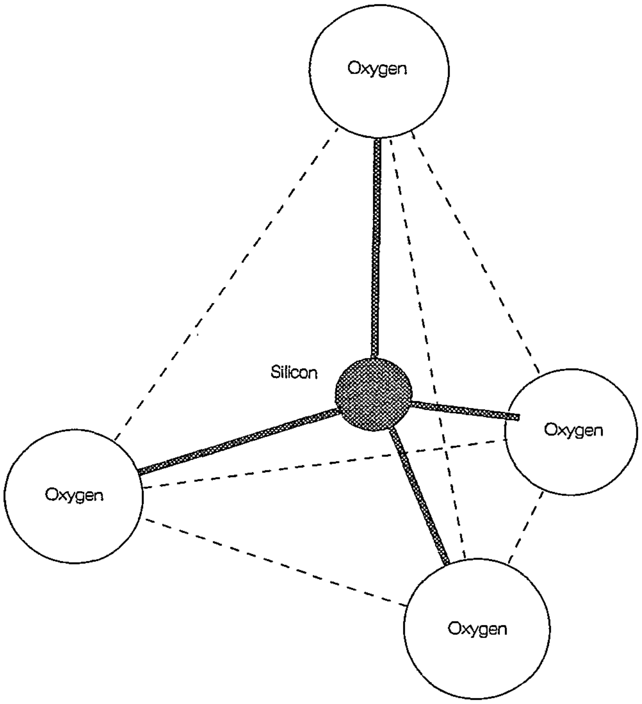

Figure 2-1. Silicon-Oxygen Tetrahedron (McLellan and Shand, 1984)

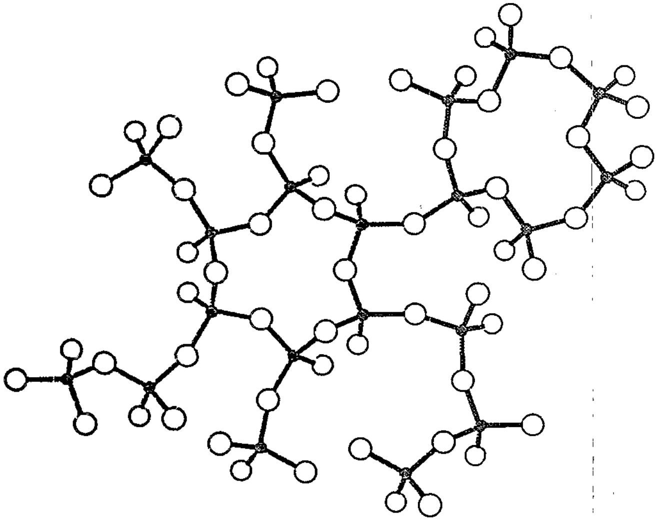

Figure 2-2. Example Silicate Glass Network Structure (McLellan and Shand, 1984)

glass and thus interrupt tetrahedra linking and the continuity of the network. An oxygen atom ionically bonded to another atom is called nonbridging.

Appreciable amounts of most inorganic oxides can be incorporated into silicate glasses. Elements that can replace silicon are called network formers. By replacing silicon in the glass network, some inorganic species (such as some metals found in the middle portion of the periodic table) can be incorporated into a glass. Most monovalent and divalent cations (such as sodium, calcium, and some other metals and metalloids grouped near either side of the periodic table) do not enter the network, but form ionic bonds with nonbridging oxygen atoms, and are termed network modifiers. The effect of variation in the network integrity and the constituents of the glass are manifested in changes in glass properties such as softening point temperature and chemical durability (i.e., leachability and solubility) (McLellan and Shand, 1984).

The role of elements in the glass may vary with conditions. For example, aluminum may be a network former or a modifier depending on the ratio of aluminum to alkali and alkaline earth ions and is thus called an intermediate. The role of iron depends on redox state or oxygen availability in the molten material. For example, Fe (III) is a network former (McLellan and Shand, 1984).

Because of the network structure of glasses, it does not help to express their composition as chemical formulae. The most common way of describing glass is to list relative amounts of oxides derived from the raw materials used in a glass formulation, even though these oxides do not exist, per se, in the glass network.

Many types of glass can be formed depending on the raw materials used. The glass industry prepares special formulations to obtain glasses with properties desirable for various uses. Important considerations for the treatment of hazardous wastes include processing characteristics, such as melt viscosity and redox conditions, and product characteristics, such as durability.

Vitreous silica, the simplest glass, can be prepared by heating silica (SiO_2) above its melting point and quickly cooling to the solid state. In order to decrease the viscosity of molten glass from that of pure silica and allow it to melt at a lower temperature, it is necessary to add a flux, or network modifier, that will soften the glass by generating nonbridging oxygen atoms. Alkali metals, such as sodium, make excellent fluxes in their oxide forms.

Alkalis can be incorporated into the glass as carbonates or other salts that react, at elevated temperatures, with silica to form a siliceous liquid. The reaction of fluxes is complex, but aside from lowering the viscosity of the glass, they also have the effect of lowering the melting point of the raw material mix. This helps decrease the energy requirements of the melting process.

Unfortunately, adding alkali to the glass generally decreases its chemical resistance from that of silica glass. At high alkali concentrations, the glass will even become water soluble (the basis for the soluble silicate industry). To decrease the aqueous solubility of alkali glasses, but to maintain the lower melting points, alkaline earth fluxes may also be used. Oxides of calcium and magnesium are the most common alkaline earth or stabilizing fluxes. However, adding too much calcium can cause calcium silicates and aluminates to form and these may crystallize (devitrify) on cooling.

Soda ash (sodium carbonate) is commonly used in industry to supply alkali fluxes, while lime (calcium oxide) is commonly added to supply alkaline earth fluxes. Thus, glass made from silica and alkali and alkaline earth fluxes is commonly called soda-lime glass. Soda-lime glass is the most common type of glass, and is used in most container glass and window glass applications. The typical composition of soda-lime glass is compared with the composition of two waste glasses in Table 2-1.

Typical raw materials for industrial glass making consist of various formulations of the following main ingredients:

- Sand - SiO_2
- Feldspar - $KAlSi_3O_8$

Table 2-1. Sample Compositions of Soda-Lime Glass, Borosilicate Glass, and ISV Glass

Oxide	Typical Soda-Lime Glass[1] (wt %)	SRS Borosilicate Benchmark Glass[2] (wt %)	Sample ISV Glass[3] (wt %)
SiO_2	65-75	48.95	71.20
Al_2O_3	1-2	3.67	13.50
Na_2O	12-16	16.71	1.55
K_2O	0.1-3	0.04	2.47
MgO	0.1-5	1.66	1.87
CaO	6-12	1.13	3.58
B_2O_3	-	11.12	-
Fe_2O_3	-	8.08	4.63
FeO	-	0.89	-
La_2O_3	-	0.41	-
Li_2O	-	4.28	-
MnO	-	1.34	0.11
NiO	-	0.61	0.12
TiO_2	-	0.71	0.76
ZrO_2	-	0.41	0.07
SrO	-	-	0.02
BaO	-	-	0.10

[1] From McLellan and Shand, 1984.
[2] From Goldston and Plodinec, 1991.
[3] This glass was produced by ISV of INEL soils. From Farnsworth, Oma, and Reimus, 1990.

- Dolomite - $CaMg(CO_3)_2$
- Limestone - $CaCO_3$
- Soda ash - Na_2CO_3

These are mixed with a variety of other constituents to produce glasses with whatever physical and chemical properties manufacturers may desire, such as heat resistance, chemical inertness, various optical properties, various colors, etc. The selection of materials from which to make a waste glass, on the other hand, generally involves compromises based on the product and processing characteristics desired.

While soda-lime glass may serve as a waste glass, many waste glasses are borosilicate glasses and contain B_2O_3. Waste glasses also generally contain less silica and more aluminum and iron than soda-lime glasses. Most soils and the ISV glass derived from their melting also have more aluminum and iron and less silica and sodium than typical soda-lime glass. The "aluminum-bearing glasses" are generally more typical of glass compositions produced in waste vitrification.

It is interesting to note that many metals of environmental concern are readily incorporated into a glass matrix and are commonly used as colorants in glassmaking. This suggests that vitrification processes may be particularly attractive for immobilizing metals found in certain waste streams. Table 2-2 presents a list of metal compounds commonly used as glass colorants.

2.2 Stabilizing Mechanisms

Hazardous constituents can be immobilized in vitrification processes by two main interactions with the glass matrix:

- Chemical bonding
- Encapsulation

Certain inorganic species can be immobilized by chemical bonding with the glass-forming materials, particularly silica, present in the wastes to be vitrified. The most notable chemical bonding within a vitrified material occurs when certain metals or other inorganics bond covalently with the oxygen atoms in a silica network and thus become part of the network. Inorganics that interact in this way are network formers since they essentially replace silicon in the glass network structure.

Other inorganic species can bond ionically with oxygen or other elements in the glass network. This ionic bonding incorporates the material into the glass but disrupts the network's continuity, thereby modifying the vitrified material's physical and chemical properties. As mentioned earlier, materials that interact in this fashion are called network modifiers.

Hazardous constituents may also be immobilized without direct chemical interaction with the glass network. Since vitrification constitutes a molten phase during some portion of the process, materials that do not interact chemically or have not completely entered solution can be surrounded by a layer of vitrified material and encapsulated, as the melt cools. This layer of vitrified material protects the encapsulated constituents from chemical attack and inhibits their ability to escape from the vitrified product (McLellan and Shand, 1984).

2.3 Chemical Attack Mechanisms

Vitreous materials are often thought of as being "inert," which is somewhat justified since these materials exhibit high corrosion resistance compared with many other materials. It is important to note, however, that all vitrified products are chemically reactive to some degree. This section discusses the nature of chemical attack on vitreous silicate materials and the factors that affect the rate and degree of attack.

There are two major forms of chemical attack on vitrified materials:

- Matrix dissolution
- Interdiffusion

2.3.1 Matrix Dissolution

Matrix dissolution is characterized by alkali attack. It begins by hydration of the silica network and may proceed to dissolution of the vitreous material. In pure silica glass, the matrix dissolution process can be described by the following equation:

$$2\,NaOH + SiO_2 \rightarrow Na_2SiO_3 + H_2O$$

The alkali silicate (Na_2SiO_3 in the example shown) is water soluble, so as the silica network is attacked and dissolved congruently, the other constituents in the vitrified material are released. The rate of alkali attack is generally linear with time; however, the rate can change if soluble materials accumulate in solution, or if insoluble reaction products adhere to the material's surface, blocking the reaction.

Table 2-2. Inorganic Colorants for Glass (Tooley, 1984)

	Color Produced	
Material	Under Oxidation	Under Reduction
Cadmium Sulfide	None	Yellow
Cadmium Sulfide, Selenium	None	Ruby
Cobalt Oxide	Blue-violet	Blue-violet
Copper Oxide	Greenish blue	Greenish blue
Cuprous Oxide	Greenish blue	Ruby
Cerium Oxide	Titania Yellow	Yellow
Chromic Oxide	Yellowish green	Emerald green
Gold	Ruby	
Iron Oxide	Yellowish green	Bluish green
Manganese dioxide	Amethyst to purple	None
Neodymium oxide	Violet	Violet
Nickel oxide	Violet in K_2O glass	Violet in K_2O glass
Nickel oxide	Brown in Na_2O glass	Brown in Na_2O glass
Selenium	Fugitive	Pink
Sulfur	None	Yellow to amber
Uranium	Yellow with green fluorescence	Green with fluorescence

Alkali attack is highly pH dependent. The rate of attack generally increases by a factor of 2 to 3 for each pH unit increase. The influence of temperature on the rate of alkali attack follows an Arrhenius relationship with the rate of attack increasing by a factor of 2 to 2.5 for each 10° C temperature rise.

2.3.2 Interdiffusion

Interdiffusion is typified by acid attack on vitrified materials. While alkali attack (matrix dissolution) leads to surface dissolution of the vitreous material, interdiffusion is an ion exchange process which preferentially extracts elements present as network modifiers, leaving the silica structure almost intact. Generally, interdiffusion involves the exchange of hydronium ions in solution for ionically bonded elements in the vitreous network (McLellan and Shand, 1984).

Interdiffusion has sometimes been called leaching, but interdiffusion is the more precise term. "Leaching" is commonly used to denote loss of constituents from a material without specifying a mechanism. As used here, interdiffusion is a mechanism; thus, to call it "leaching" is confusing.

The reaction rate in interdiffusion is influenced by temperature in a relationship similar to that for alkali attack; however, the interdiffusion reaction rate increases only by a factor of 1.5 to 2 for each 10°C temperature rise.

Depending on the composition of the vitrified material, especially its silica content, the pH of the leaching solution influences the rate of acid attack. Generally, that influence is not as strong as the influence on the rate of alkali attack.

The rate of acid attack on glass is generally proportional to the square root of time. Since the process is controlled predominantly by diffusion, the rate of leaching decreases as the thickness of the leached layer near the glass surface increases. However, this effect can be limited if the layer dissolves or sloughs off.

The leachability of trace constituents is difficult to predict, but it is reasonable to assume that in addition to the alkali and alkaline earth elements (sodium, potassium, calcium) there may be preferential extraction of other network modifiers of potential environmental concern, such as: barium (Ba), beryllium (Be), cobalt (Co), copper (Cu), lead (Pb), magnesium (Mg), manganese (Mn), nickel (Ni), silver (Ag), strontium (Sr), and zinc (Zn).

Water attacks vitrified materials to some degree, although the attack is much less aggressive than that of alkali and is generally less vigorous than acid attack. Water can exhibit both acid and alkali attack mechanisms since it can produce both hydronium and hydroxyl ions. However, in a static environment water attack quickly becomes alkali attack as the alkali present in the glass is extracted into the water and then takes part in the reaction.

Attack by salt solutions is thought to correspond to the attack by water, but the mechanism has not been thoroughly defined. However, typical attack rates at room temperature are still very low. Many chelating compounds attack glasses at a rate comparable to that of strong alkali. Citrate, gluconate, oxalate, tartrate, EDTA, and malate all attack glass in alkaline solution. Alkaline phosphate and acetate also attack glass readily. Hydrofluoric acid has a unique ability to dissolve silicate glasses, forming a solution of alkali fluorides and silicon fluorides.

2.3.3 Three -Stage Model of Waste Glass Corrosion

While dissolution and interdiffusion describe leaching under many conditions, the leaching of many waste glasses appears to be modified by the formation of surface gel layers (Wicks, 1985). Layer formation is favored in static or near-static conditions and where silica is present, as in many groundwaters. As matrix dissolution occurs, the surface layers, composed of insoluble glass components, arise. The formation of these layers proceeds in a three-stage process.

Stage one is dominated by interdiffusion as network modifiers, such as sodium, diffuse out of the glass and into solution, and water diffuses in. The result is a modifier- deficient surface layer. During this stage the pH of the leachant increases (becomes more basic), because alkali hydroxides form in solution.

Stage two is dominated by matrix dissolution. As described earlier, matrix dissolution is an alkaline attack; thus, its rate is primarily governed by the pH of the leachate, glass composition, and temperature.

Stage three is characterized by the formation of surface layers. These surface layers are formed from the precipitation and adsorption of insoluble compounds onto the surface of the glass. These compounds are the more insoluble waste glass constituents that are "left behind" as more soluble constituents dissolve and move into solutions. For example, these surface layers may contain substantial iron and manganese hydroxides. Where a surface layer forms, it can exert a strong limiting effect on leaching of the waste glass underneath. Under static or near-static conditions, leaching may be reduced further as silica concentrations build up in the leachate and approach saturation, thus reducing even more the tendency of silica in the glass to move into solution.

2.3.4 Factors Impacting Waste Glass Leaching

The use of vitrification to treat HLW has produced a wealth of knowledge about waste glasses and their production, particularly in terms of chemical composition, waste loading, temperature, time and pH.

Chemical Composition. Chemical composition plays an important role in product durability (Wicks, 1985). In general, as the ratio of oxygen to network formers (such as silicon) decreases, more bridging oxygens are produced, resulting in a more durable product. Network modifiers such as alkalis and alkali earth oxides tend to decrease glass durability. This occurs because these oxides increase the oxygen-to-network former ratio and produce more singly-bonded oxygen, thus breaking up the glass network. However, these elements do lower melt viscosity and lower processing temperatures and therefore have potential as fluxing agents. In general, oxides with valences greater than 1 may increase glass durability.

Composition of the incoming feed can have enormous effects on product durability and processing parameters. Table 2-3 displays some of the effects of various inorganic oxides on processing and glass durability. Modification of the waste stream through additives and/or material removal can have dramatic impacts on processing and product characteristics. However, as Table 2-3 shows, most additives have both desired and undesired effects. Therefore, modification of the feed will often involve compromises based on treatment goals, processing limitations, and waste character.

Waste Loading. Increased waste loading does not necessarily increase product leachability (Wicks, 1985; Mendel, 1973). Research on borosilicate glass for the immobilization of nuclear waste has indicated that glass leachability is reduced as the waste loading increases from 0 wt% to 35 wt%, with only small changes in leachability as the waste loading increases from 35 wt% to 50 wt% (Rankin and Wicks, 1983). Thus, the amount of waste immobilized by borosilicate glass may not be limited by product durability, but by processing considerations. The reason for the beneficial effects of increased waste loading on durability is due to the formation of surface layers that form during leaching and that are made up of the major constituents found in the waste composition.

Temperature. Leachability of waste glass increases with temperature (Wicks, 1985). The mechanism of corrosion varies with temperature: at temperatures near ambient conditions, diffusion effects can dominate glass corrosion, but at temperatures near 100°C or higher, network dissolution can dominate. The exact temperature for the shift in mechanism varies with test conditions and glass composition.

Time. At a given temperature, the largest leach rates occur during the early stages of leaching (Wicks, 1985). Therefore, leach rates usually decrease over time. Two mechanisms appear to be involved in this leach rate decrease. First, under static or near static conditions, such as groundwater in proposed repositories, the solution becomes saturated as elements are extracted from the glass and enter solution. Increased saturation reduces the solution's solubility and its ability to corrode the glass. Secondly, with time, a layer forms on the glass's surface, thereby further inhibiting leaching (Jantzen, 1988).

pH. In solutions of about pH 3 to 9, glass leaching may be substantially or minimally affected by solution pH, depending on the chemical composition of the glass (Wicks, 1985). At pH values above 9 (basic conditions), two mechanisms function to increase leaching: silica solubility increases and matrix dissolution dominates. The effect of acidic conditions on glasses varies more than the effect of basic conditions. Most silicate glasses are dominated by interdiffusion at low pH values. For these glasses, leach rates are proportional to the square root of time and the effect of low pH values is small. However, borosilicate glasses are dominated by matrix dissolution at low pH values. Their leach rate increases linearly with time and the effect of acid attack (below pH 5) may be quite dramatic. Thus, the expected pH of the disposal site or use location may be important in determining the desired composition of the waste glass.

Table 2-3. Effects of Waste-Glass Components on Processing and Product Performance (adapted from Plodinec, Wicks, and Bibler,1982).

Frit Components	Processing	Product Performance
SiO_2	Increases viscosity greatly; reduces waste solubility	Increases durability
B_2O_3	Reduces viscosity; increases waste solubility	Increases durability in low amounts, reduces in large amounts
Na_2O	Reduces viscosity and resistivity; increases waste solubility	Reduces durability
Li_2O	Same as Na_2O, but greater effect; increases tendency to devitrify	Reduces durability, but less than Na_2O
K_2O	Same as Na_2O; decreases tendency to devitrify	Reduces durability more than Na_2O
CaO	Increases then reduces viscosity and waste solubility	Increases then reduces durability
MgO	Is same as CaO; reduces tendency to vitrify	Is same as CaO, but more likely to decrease durability
TiO_2	Reduces viscosity slightly; increases then reduces waste solubility; increases tendency to devitrify	Increases durability
ZrO_2, La_2O_3	Reduces waste solubility	Increases durability greatly
Waste Components	Processing	Product Performance
Al_2O_3	Increases viscosity and has tendency to devitrify	Increases durability
Fe_2O_3	Reduces viscosity; is hard to dissolve	Increases durability
U_3O_8	Reduces tendency to devitrify	Reduces durability
NiO	Is hard to dissolve; increases tendency to devitrify	Reduces durability
MnO	Is hard to dissolve	Increases durability
Zeolite	Is slow to dissolve; produces foam	Increases durability
Sulfate	Is an antifoam, melting aid; increases corrosion of processing equipment	Too much causes foam or formation of soluble second phase

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) 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.

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)

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.

<u>Mechanical Constraints</u>. 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, annodization 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).

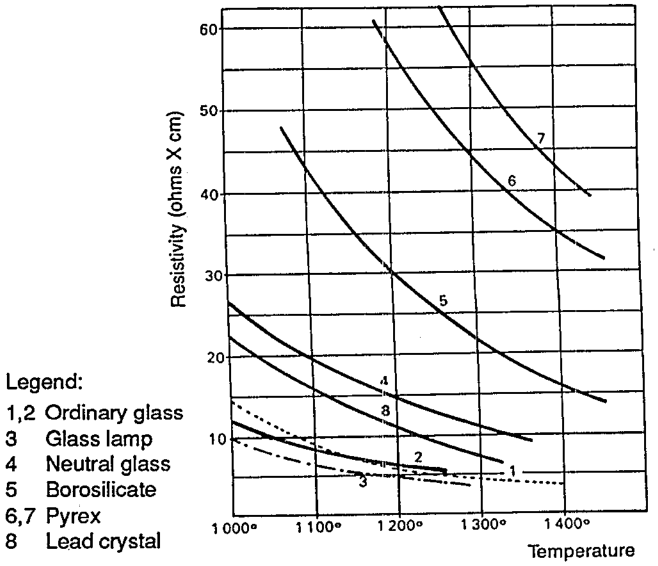

Figure 3-1. Relationship Between Resistivity and Temperature for Selected Glasses (Orfeuil, 1987)

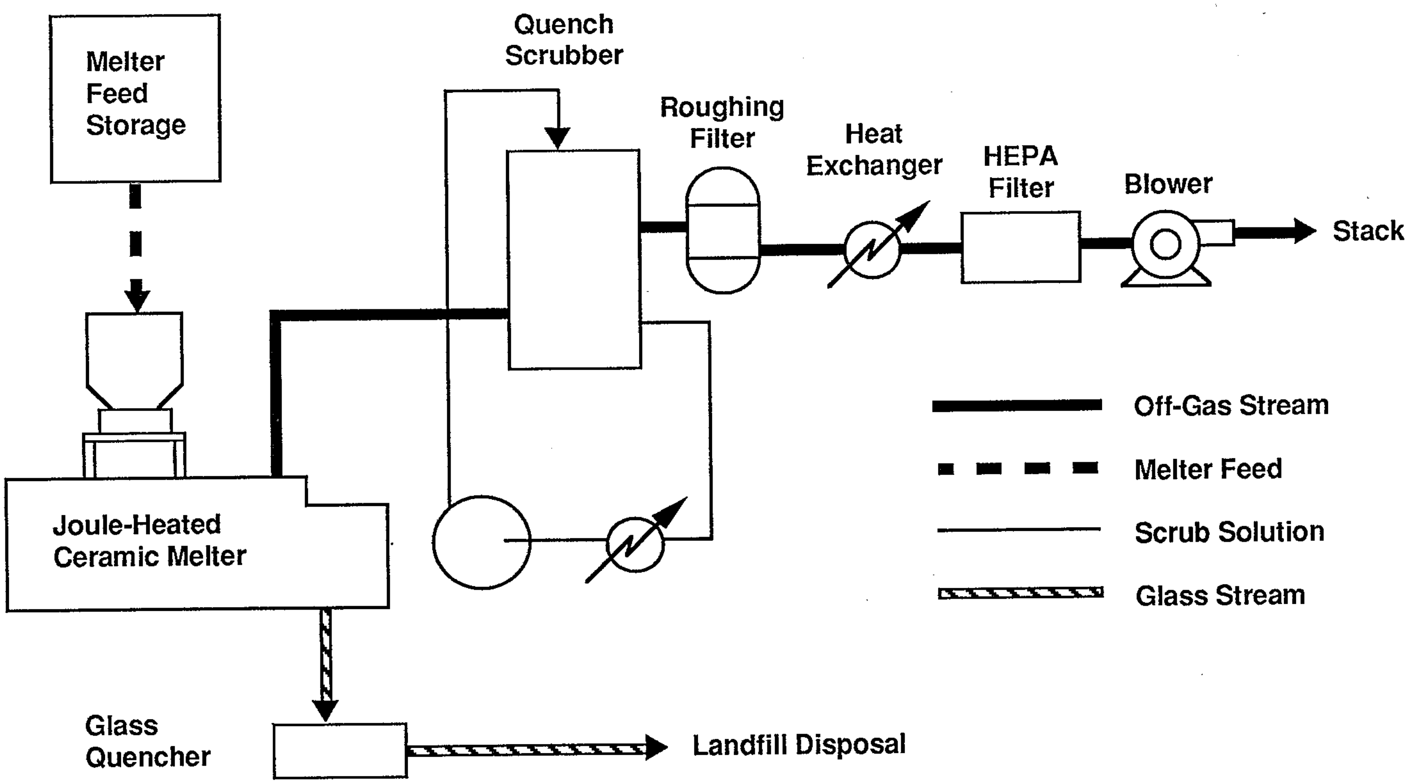

Figure 3-2. Typical JHCM Process Flowsheet (adapted from Koegler et al., 1989)

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.

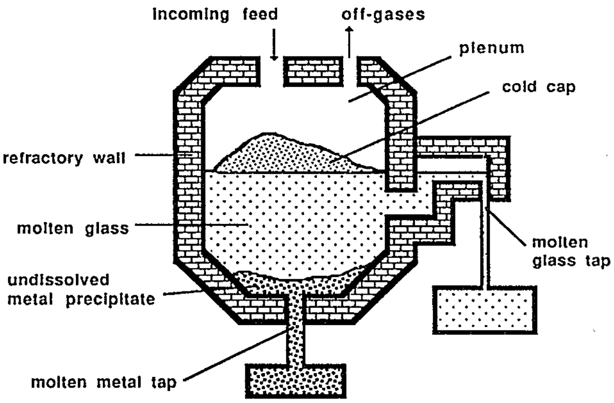

Figure 3-3. Generalized JHCM Showing Components of Melter and Molten Material

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 pyrolized by-products migrate to the surface of the vitrified 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

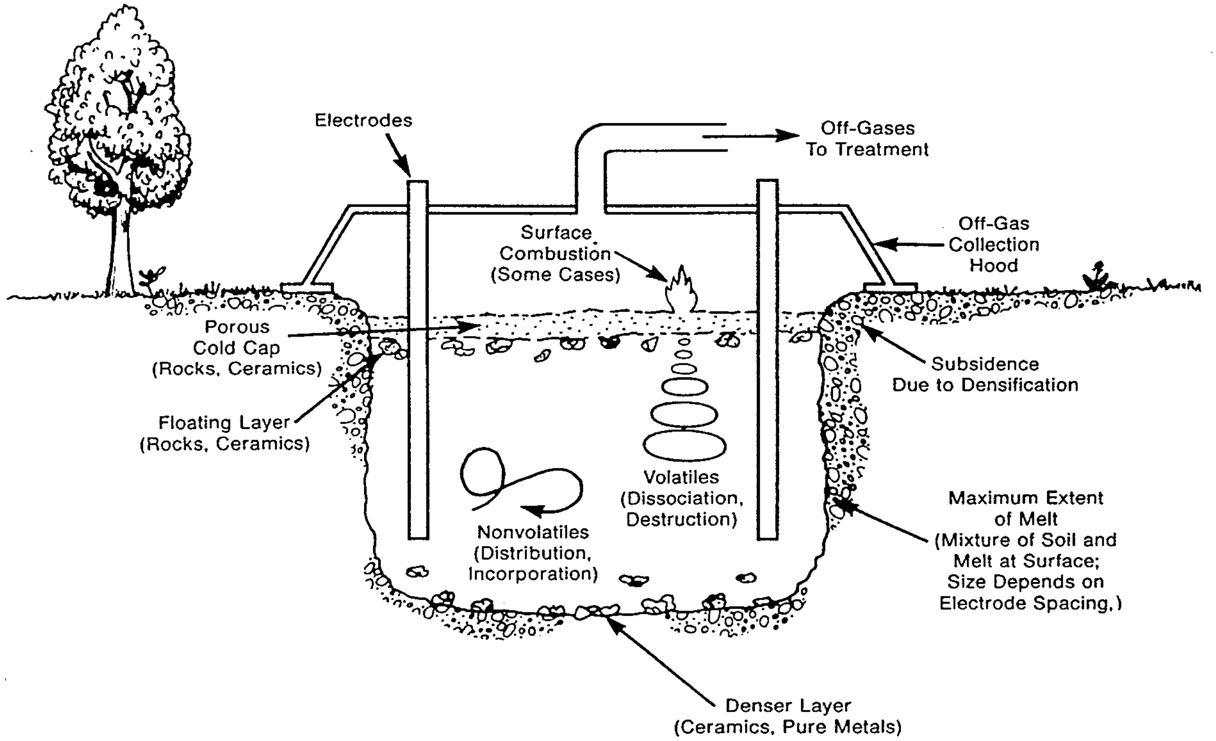

Figure 3-4. Schematic of ISV (adapted from USEPA, 1989b)

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 (Koegler 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-

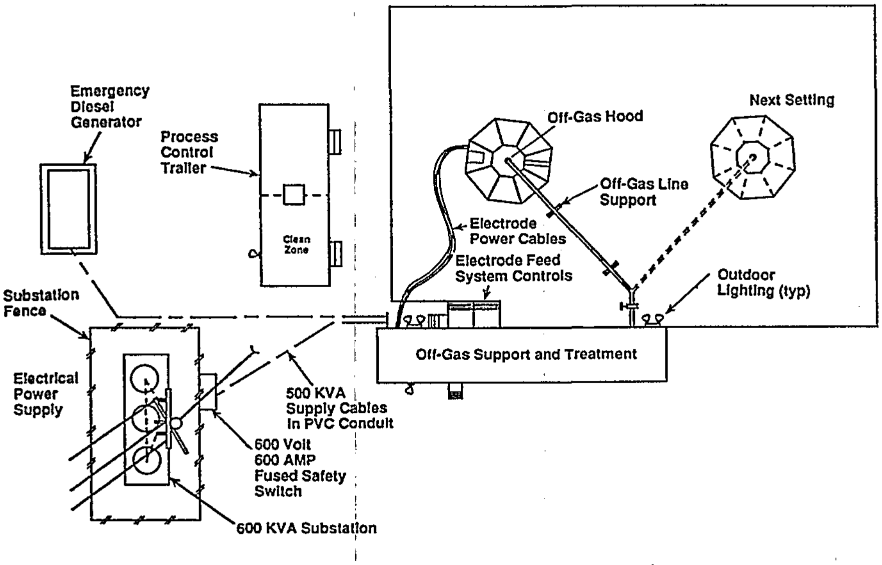

Figure 3-5. Pilot-Scale Process ISV (adapted from Callow, Weidner, and Thompson, 1991)

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. Kupp, 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

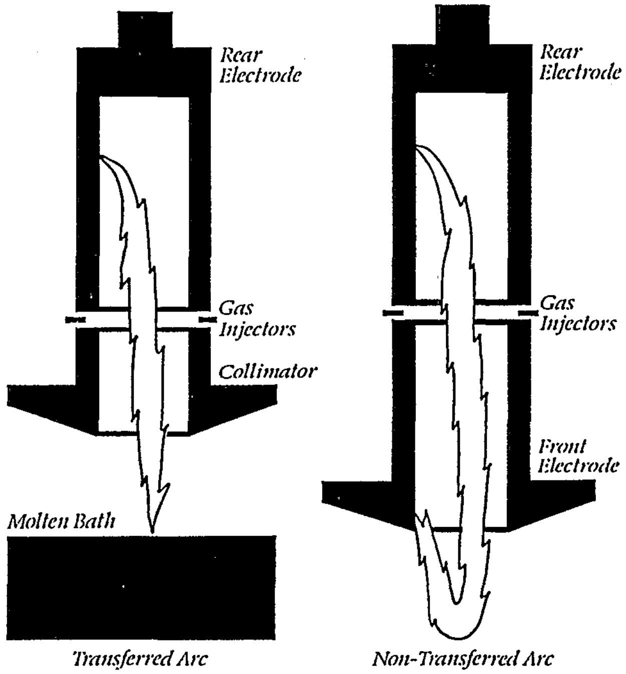

Figure 3-6. Comparison of a Transferred Arc and a Non-Transferred Arc (Source: Plasma Energy Corporation)

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°C, heats the waste material beyond the point of melting to about 1,600°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

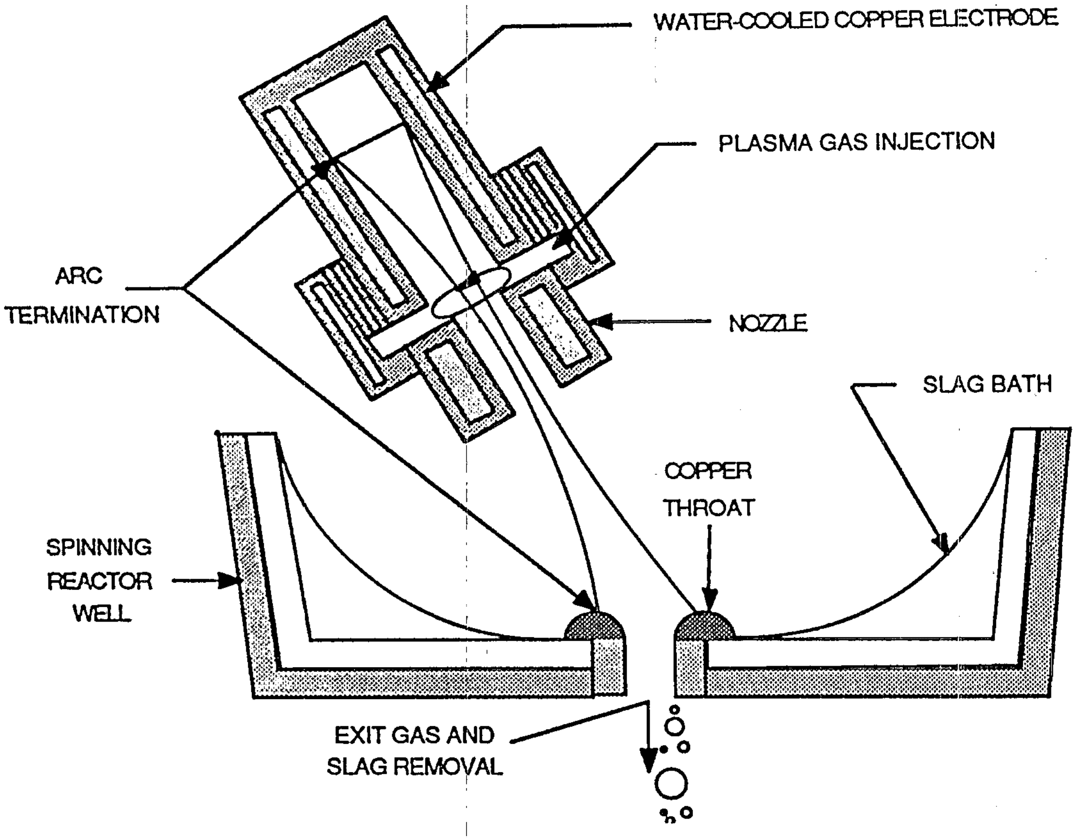

Figure 3-7. Schematic of the Demonstration PCR Showing the Bottom-Pour Configuration for Exit Gas and Molten Glass (Eschenbach, Hill, and Sears, 1989)

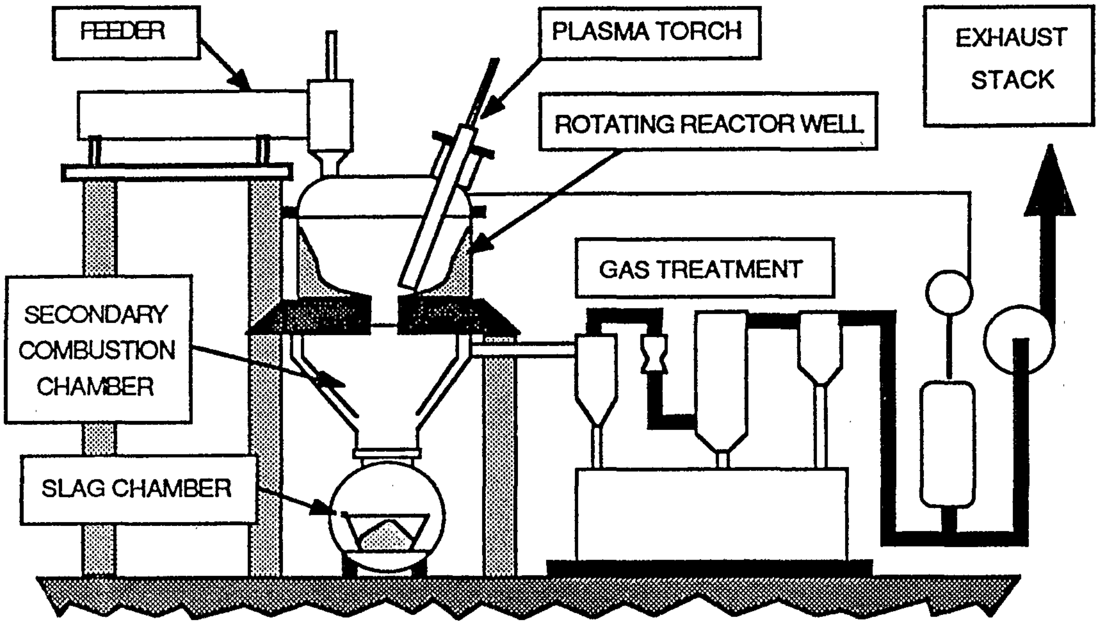

Figure 3-8. Schematic of a Full-Scale PCR (Eschenbach, Hill, and Sears, 1989)

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 (PWTF) 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

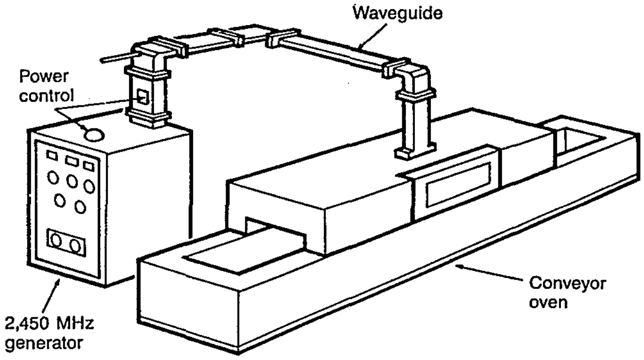

Figure 3-9. Microwave Melter (Orfeuil, 1987)

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 difficulty 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 descendents. 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 m^3 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, afterburner, 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.

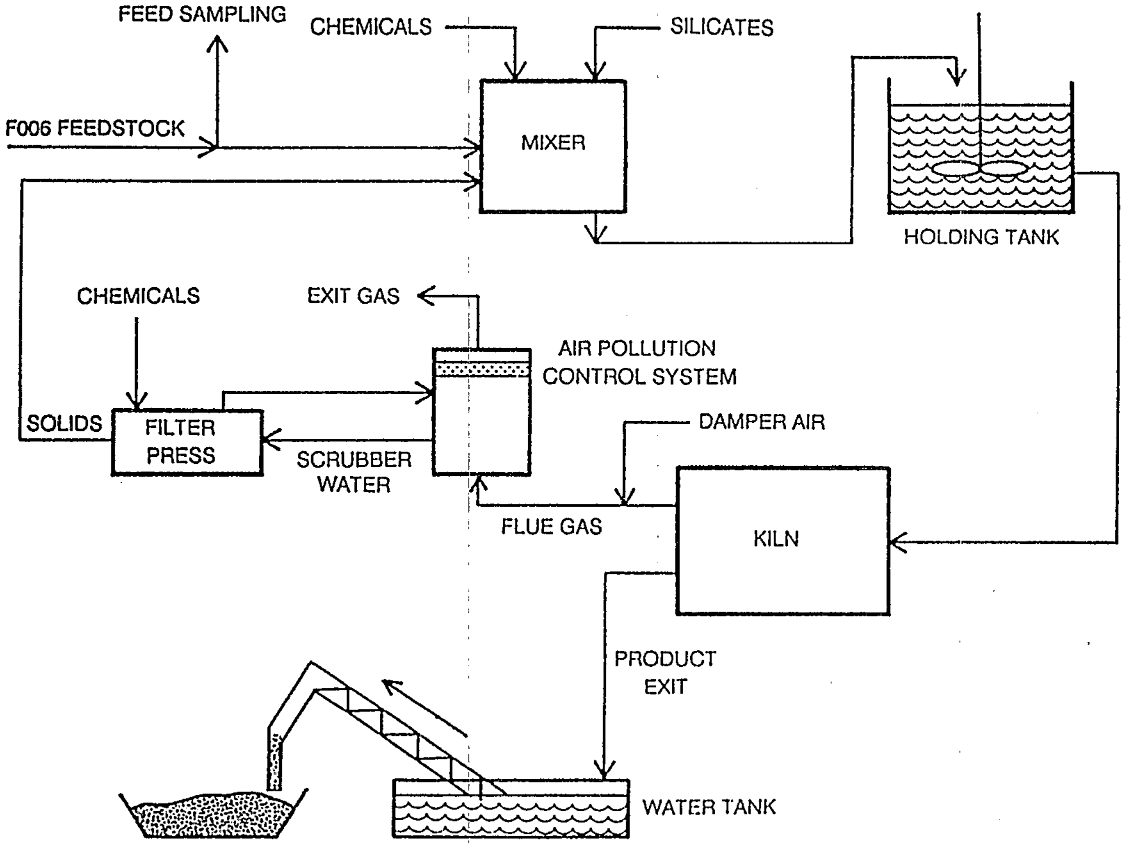

Figure 3-10. Flow Diagram of the IRI Process (adapted from *The Hazardous Waste Consultant*, 1990a)

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.

Gases travel up the kiln and enter the off-gas treatment system where the remaining organic materials may be destroyed thermally (temperatures range from 870 to 1260°C) in a series of oxidizers (Harlow et al., 1989).

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 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).

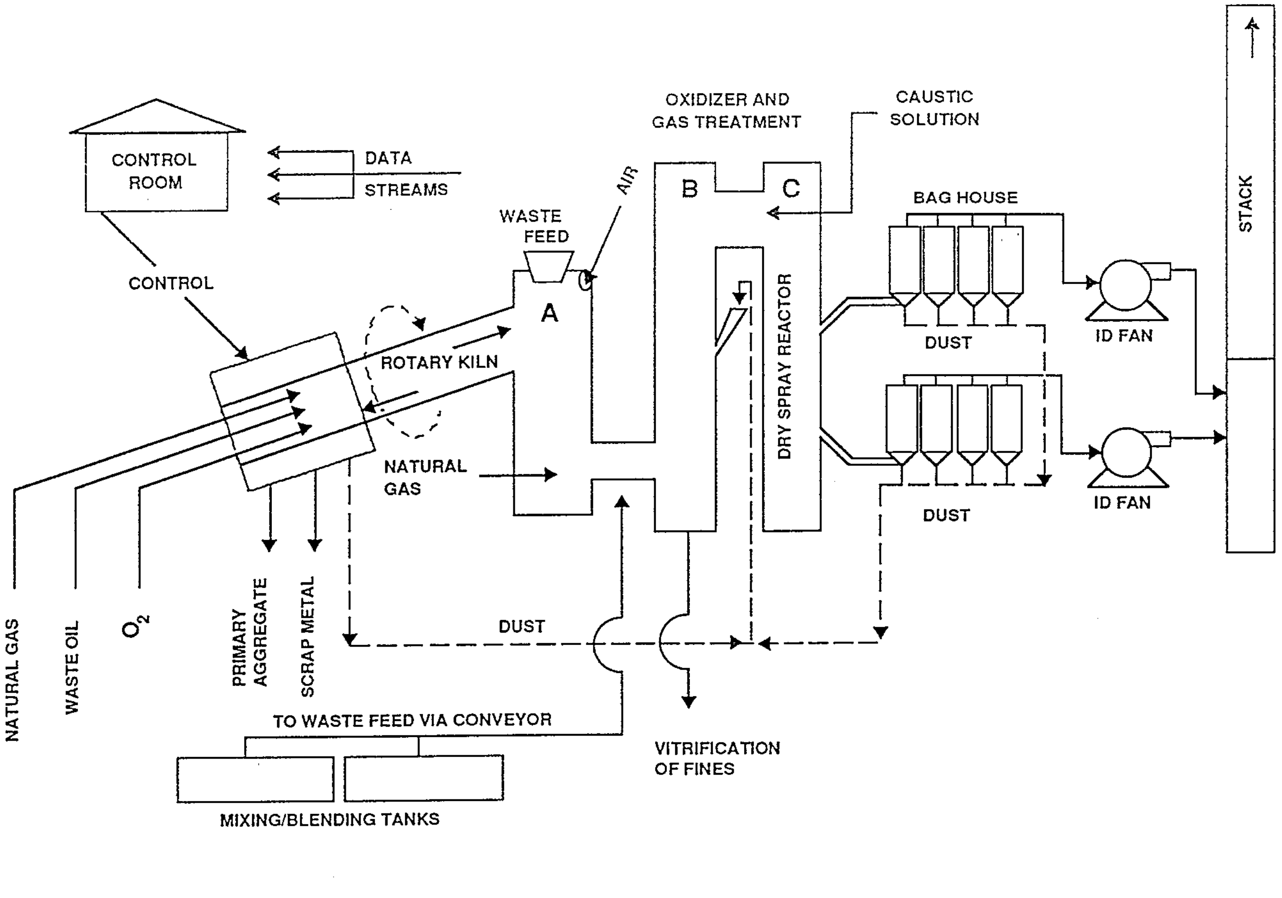

Figure 3-11. Simplified System Schematic of MSP's Process (adapted from Harlow et al., 1989)

CHAPTER FOUR

APPLICABLE WASTE TYPES AND CONTAMINANTS

This chapter discusses waste and contaminant types to which vitrification applies. The wastes and contaminants identified here are not inclusive. Vitrification potentially applies to a very wide variety of wastes and contaminants. As Chapter One made clear, inclusion of a waste and a contaminant in this chapter does not mean that vitrification is the preferred technology for this waste at all sites. Furthermore, inclusion is not meant to suggest that all the technical problems for application have been solved, or even that they will be solved. The tests and studies included in this chapter serve to indicate the potential of vitrification for consideration in early screening studies.

4.1 Applicable Waste Types

Some vitrification processes may be able to handle a wide variety of waste types, while others are applicable only to a very specific waste stream. Wastes to which vitrification potentially applies include:

- Radioactive wastes and sludges
- Contaminated soils
- Contaminated sediments
- Incinerator ashes
- Industrial wastes and sludges
- Medical wastes
- Underground storage tanks (USTs)
- Drummed wastes
- Shipboard wastes
- Asbestos wastes

Radioactive Wastes and Sludges. The global implementation of vitrification to treat nuclear wastes demonstrates vitrification's potential for this waste type. Mixed wastes, in which radioactive contaminants are combined with Resource Conservation and Recovery Act (RCRA) hazardous inorganic and/or organic contaminants, also pose a challenge to remediation and/or disposal. Because vitrification may destroy organics and incorporate inorganics, it may be applicable at sites with difficult wastes such as mixed wastes.

Radioactive inorganic contaminants are not destroyed during vitrification, but, as most are metals, are generally incorporated in the glass during vitrification. Thus, vitrification puts them in a waste form which is more manageable and decreases the probability of their escape into the environment. The discussion of metal inorganics (later in this chapter) will address the fate of radioactive contaminants more fully.

Radioactive sludges (or slurries) will be the incoming feed for the LFCM vitrification at West Valley, New York, and the Savannah River Site (SRS), South Carolina (Bjorklund, Mellinger, and Pope, 1984; Wicks and Bickford, 1989). At the SRS, the sludge and the supernatant salt solution from HLLW storage tanks will first be separated. Each of these waste streams will then be treated to concentrate the radioactive contaminants found in each. Prior to melting, these streams will be mixed to form the slurry that will feed the LFCM (Wicks and Bickford, 1989).

Contaminated Soils. Treatment of contaminated soils has been proposed for all types of vitrification processes. Generally, soils are amenable to vitrification since they often contain high percentages of silica, alumina, and other glass-forming raw materials. Soil composition will impact product characteristics such as density and chemical durability. Soil composition will also impact processing parameters by helping to define thermal conductivity, fusion temperature, specific heat, electrical conductivity, and melt viscosity (Buelt et al., 1987).

PNL evaluated soils across the United States and felt that most were amenable to ISV (Shelley, 1990). The primary soil characteristics limiting ISV application are high quartz content and low alkali flux content without flux addition. Other vitrification processes should also be applicable to a variety of soils. In fact, the various ex situ processes may be better able to vitrify a variety of soils because of the greater ease with which incoming soil can be modified through feed additives.

Site characteristics and treatment objectives will play an important role in determining which type of vitrification process, if any, is applicable. Chapter Seven discusses in more detail the limitations placed on vitrification by site characteristics.

One important issue in the application of ISV to contaminated soils is whether volatile organic contaminants migrate away from the melt, or are captured by the melt and destroyed. This issue will be addressed later in this chapter.

Contaminated Sediments. As most sediments are composed of run-off soils and other components amenable to vitrification, vitrification should be applicable at many sites with contaminated sediments. However, sediments generally have high moisture contents. Any material with high water content increases processing time and energy demands by first requiring that the water be driven off. Thus, vitrification may be limited economically in its ability to treat sediments. If vitrification is to be used to treat sediments, the demands on time and energy need to be addressed. This is generally accomplished by dewatering or drying prior to vitrification.

ISV engineering-scale tests have been performed on polychlorinated biphenyl (PCB) contaminated sediments from New Bedford Harbor. Results indicated destruction and removal efficiencies (DRE's) of greater than 99.99999%. TCLP testing resulted in leach extract that contained metal concentrations below the regulatory limits (Reimus, 1988).

Incinerator Ashes. While incineration significantly reduces volume of waste materials, the resulting ash may concentrate undesirable inorganics and heavy metals. Vitrification further reduces ash volume, destroys residual organics, and immobilizes heavy metals. In addition, the vitrified ash may become a useful construction material and thus avoid the need to landfill the ash (Chapman, 1991). Treatment of incinerator ash is one of the growing areas of interest in vitrification. In Japan, the aggregate produced in the vitrification of incinerator ash is used in road construction (GRI, 1989). Vitrification is potentially applicable to the ash from MSW incinerators, hazardous waste incinerators, and other incinerators. Both bottom ash and fly ash may be amenable to vitrification.

Firms in Europe are increasingly looking to vitrification to deal with the ash from hazardous waste incinerators. Tougher pollution control legislation, the expense and regulations involved in landfill disposal, and the closing of international borders to the importation of hazardous wastes are all helping to make vitrification cost effective as the tail end of a treatment train focusing on incineration as the main agent of toxin destruction (Gilges, 1991). In the United States, Recomp of Washington (ROW) opened a facility in 1991 to vitrify MSW incinerator ash. Feasibility studies in preparation for this facility have indicated an 80% volume reduction of the ash (Chapman, 1991).

Used in the context described above, vitrification no longer functions as a stand alone technology, but rather as part of a treatment train. Darnell (1990) proposed that vitrification be used in a treatment train preceded by incineration and followed by solidification.

Industrial Wastes and Sludges. Because of vitrification's ability to immobilize inorganics, it is considered for the treatment of industrial waste streams containing contaminant metals. The United States Army Toxic and Hazardous Materials Agency (USATHMA), for example, has conducted bench-scale studies on the vitrification of paint sludge wastes and found vitrification to be applicable to these (Balasco et al., 1987). The vitrification system of IRI handles liquid, solid, or sludge type inorganic feedstock input such as metal-bearing sulfates, metal-bearing carbonates, and metal-bearing phosphates. The IRI system has been tested and has produced a potentially usable product for the following EPA listed waste streams: F006 (electroplating wastes); K061 (electric arc furnace ducts); and D004 through D006 (inorganic transition metals, arsenic (As), barium (Ba), cadmium (Cd), chromium (Cr), and lead (Pb)); (*The Hazardous Waste Consultant*, 1990a).

As with sediments, industrial sludges are vitrifiable, but water content may increase processing costs. Tests of ISV with zirconia-lime sludges showed that the material was vitrifiable and that the level of radon emanation was reduced by a factor of 10^4 to 10^5 after processing. Measured radon emanation rates were in the femtocurie range (Buelt, Timmerman, and Westsik, 1989).

Medical Wastes. The vitrification of medical wastes may destroy potential pathogens, provide very large volume reductions, and immobilize any metals. A plasma heating system using a non-transferred arc has been tested on medical wastes by Aerospatiale. Results indicated a very low (0.25%) concentration of unburned waste in the solid residue and no biological activity in the ashes.

Underground Storage Tanks. USTs containing sludges and salt cakes of radioactive and/or hazardous chemicals are present at many DOE sites. Recent enactment of stringent environmental regulations requires timely remediation of certain inactive tanks. Studies evaluating tank remediation alternatives show that many of the tanks may potentially be treated in place using ISV, although significant technical issues need to be resolved. Tanks containing material that cannot be economically removed and tanks with outlying soil contamination are likely candidates for in-place treatment by ISV (Campbell, Timmerman, and Bonner, 1990).

The ISV of USTs proceeds by filling the tanks with clean or contaminated soil and then melting the tank, the tank contents, and the surrounding soil. Processing results in the vitrification of tank wastes and the surrounding contaminated soil. The tanks themselves form a metal ingot at the bottom of the melt upon cooling (Campbell, Timmerman, and Bonner, 1990).

So far, researchers have tested the applicability of ISV to USTs at three levels: engineering-scale, pilot-scale, and large-scale.

The engineering-scale test was conducted on a 30 cm steel tank coated with concrete. The tank contained a sludge made of the contents from ORNL USTs. Contaminants included uranium (U), technetium (Tc), lead (Pb), mercury (Hg), chromium (Cr), cesium (Cs), and strontium (Sr). The tank, contents, and surrounding soil were all vitrified.

The pilot-scale test was conducted on a 1 m steel tank coated with concrete. The tank contained a 35-cm-deep sludge layer containing hazardous wastes typical of a "worst case" scenario for ORNL inactive USTs. Both the glass and metal products produced in this test passed the TCLP (Campbell, Timmerman, and Bonner, 1990).

PNL completed a large-scale test of a 6000-gallon, 10-foot-diameter, steel and concrete UST in July of 1991. The tank did not contain hazardous or regulated materials but did contain a layer of water saturated soil, with the balance of the tank filled with pumice. The test was terminated earlier than planned when a sudden release of water vapor caused the containment hood to pressurize. Since gas and vapor generated below the melt inside the confines of the tank can only escape by venting through the melt, it was discovered that under these conditions, unpredictable, sudden releases of steam or vapor can cause the containment hood to pressurize. Consequently, a key understanding of this behavior and identification of potential methods to deal with it is necessary to mitigate the consequences of gaseous releases under these conditions.

Drummed Wastes. Vitrification is attractive for treating drummed waste because the drums, as metals, may be incorporated into the waste glass. At least three processes have developed methodologies for treating drummed wastes: MSP, Retech and ISV. In the MSP process, liquids are removed from the drummed materials and used as supplementary fuels. The sludges and solids in the containers and the shredded containers themselves are blended to create a waste feed to a rotary kiln (Harlow et al., 1989). The Retech process is similar in that liquids are first removed and fed separately to the furnace. The partially emptied drums are shredded in the furnace above the melt using a copper electrode that creates an arc with the drum. This arc melts and cuts the drum at the arc contact point. Contents remaining in the drum fall into the melt as the drum is shredded. Eventually, all the pieces of the drum itself fall into the melt chamber and are incorporated into the melt (Schlienger and Eschenbach, 1991). While not ready for wholesale remediation of drummed waste, ISV has been used to process drummed waste in tests. It may also be possible to add intact, filled drums along with other trash to a properly designed ex situ vitrification system.

Shipboard Wastes. Concerns governing the disposal of wastes at sea are driving the re-evaluation of waste disposal options for shipboard wastes. Vitrification offers a volume reduction of wastes and a chemically durable product that may potentially be dumped overboard. Because of these attractive benefits, the U.S. Navy is examining this option. Furthermore, Penberthy Electromelt, Inc. is marketing a version of their glass melter for shipboard vitrification. However, no vitrification units are known to be presently operating on board a ship.

Asbestos Wastes. Asbestos frequently contaminates a wide variety of materials. Asbestos-contaminated materials are amenable to vitrification because it thermally destroys asbestos. Vitrification of asbestos is described in greater detail later in this chapter.

4.2 Applicable Contaminants

Vitrification is potentially applicable to a wide range of organics and inorganics, including both radioactive contaminants and asbestos. Because vitrification may immobilize inorganics and destroy organics, it is also applicable to wastes with organic and inorganic compounds.

Vitrification has four possible effects on contaminants:

1. Destruction through pyrolysis or combustion
2. Removal in off-gas treatment
3. Chemical and/or physical immobilization in the glass product or metal slag
4. Escape into the environment

Pyrolysis in the intense heat within the molten bath generally destroys organic wastes. Organic wastes not destroyed by pyrolysis are generally destroyed by combustion in a region separate from the melt. Most often, combustion occurs in the plenum, or the area above the melt surface, but within the furnace. For ISV, the plenum is defined as the space above ground level, but within the hood. In other processes, combustion may occur in a secondary combustion chamber. For example, in Retech's plasma heat process, combustion takes place primarily in a secondary combustion chamber adjacent to the centrifugal furnace (Eschenbach, Hill, and Sears, 1989). Organic contaminants that fail to pyrolyze or combust must be removed by the off-gas treatment system.

Pyrolysis destroys not only organics, but asbestos as well. In the melt, asbestos breaks down into its constituent groups (atoms or molecules), and these constituents are incorporated into the waste glass or removed by the off-gas system.

Metals (including radioactive metals) are not destroyed but are immobilized in the solidified glass or metal slag or are vaporized. Immobilization may occur when the contaminant is incorporated into the glass network or encapsulated (or surrounded) by the glass. These two immobilization processes also prevent some radioactive decay products from escaping into the environment. The off-gas treatment system should be designed to capture vaporized inorganics.

During ISV treatment, contaminants may migrate along three different pathways. The first pathway occurs when vitrification fails to either destroy or immobilize the contaminant and the contaminant subsequently passes through the off-gas system without being removed. The second pathway is the movement of contaminants into uncontaminated, adjacent soil during ISV. The existence and importance of this pathway are debated at present. Finally, contaminants may also migrate during excavation, transportation, pre-treatment, and other steps demanding handling of the contaminated material. Contaminant migration during material handling is a common concern for all ex situ treatments, vitrification as well as non-vitrification treatments, and so will not be addressed in this document.

Following is a discussion of the applicability of vitrification to metal and radioactive inorganics, non-metal inorganics, and organics.

4.2.1 Metal and Radioactive Inorganic Contaminants

Metals are not destroyed during vitrification; therefore, there are only three possible pathways for metals during treatment: (1) removal in the off-gas treatment, (2) chemical and/or physical immobilization in the glass product or metal precipitate, (3) escape into the environment.

Depending on treatment goals, chemical and/or physical immobilization is generally preferred to off-gas treatment. But when vitrification fails to incorporate metals into the melt, they must be removed by the off-gas system and receive additional treatment as secondary wastes. However, it is sometimes desirable not to chemically or physically immobilize metals in the vitrification process. For example, mercury is removed during pre-treatment prior to HLW vitrification at the SRS DWPF. Or, if recovery of the metals is a concern, the metals may be recovered from the off-gas system and thus reused. In this scenario, non-incorporation in the melt and removal by the off-gas system would be preferred. Recovery of mercury in this way is being explored by the Department of Defense (DOD) for remediation of the M-1 holding ponds at the Rocky Mountain Arsenal, Colorado.

Retention efficiencies vary with type of metal; different metal oxides will have different solubility limits in glass. The solubility limits of most metal oxides and salts in glass can be found in the *Handbook of Glass Manufacture* (Tooley, 1984) and other documents on glass production. Oxides for which extensive solubility information is available are: alumina, antimony oxide, arsenic oxides, barium oxide, cadmium oxide, chromium oxide, copper oxides, cobalt oxides, iron oxides, lead oxides, manganese oxides, nickel oxides, selenium oxides, tin oxides, and zinc oxides (USEPA, 1990a). Waste glass will retain metals with varying efficiency depending on the type of vitrification process used and its operating parameters. These limits will also be influenced by other metals in the waste and the chemical composition of the glass. Table 4-1 presents measured solubilities of elements in silicate waste glass. These values should be read very generally due to the multitude of processing variations which can affect element solubility.

Data for retention efficiencies of selected metals by ISV is presented in Table 4-2. ISV is not as amenable as other vitrification types to manipulation of operating parameters and so its retention factors give a rough estimate of difficult metals. For that reason, the data presented in this

Table 4-1. Approximate Solubility of Elements in Silicate Glasses (adapted from Volf, 1984)

less than 0.1 wt%:	Ag, Ar, Au, Br, H, He, Hg, I, Kr, N, Ne, Pd, Pt, Rh, Rn, Ru, Xe
between 1 and 3 wt%:	As, C, Cl, Cr, S, Sb, Se, Sn, Tc, Te
between 3 and 5 wt%:	Bi, Co, Cu, Mn, Mo, Ni, Ti
between 5 and 15 wt%:	Ce, F, Gd, La, Nd, Pr, Th, B, Ge
between 15 and 25 wt%:	Al, B, Ba, Ca, Cs, Fe, Fr, K, Li, Mg, Na, Ra, Rb, Sr, U, Zn
greater than 25 wt%:	P, Pb, Si

Table 4-2. Metals Retention Efficiency Test Results for ISV (Hansen, 1991)

Class	Metal		Retention Efficiency, % [a]	Scale[b]
Volatile	Mercury	(Hg)	0	Engineering
Semi-Volatile	Arsenic	(As)	70-85	Engineering
	Cadmium	(Cd)	67-75	Pilot
	Cesium	(Cs)	99-99.9	Pilot
	Lead	(Pb)	90-99	Pilot
	Ruthenium	(Ru)	99.8	Pilot
	Antimony	(Sb)	96.7-99.9	Pilot
	Tellerium	(Te)	50-99	Pilot
Non-Volatile	Americium	(Am)	99.99	Pilot
	Barium	(Ba)	99.9	Engineering
	Cerium	(Ce)	98.9-99.9	Pilot
	Cobalt	(Co)	98.7-99.8	Pilot
	Copper	(Cu)	90-99	Engineering
	Chromium	(Cr)	99.9	Engineering
	Lanthanum	(La)	98.9-99.98	Pilot
	Molybdenum	(Mo)	99.9-99.999	Pilot
	Neodymium	(Nd)	99-99.98	Pilot
	Nickel	(Ni)	99.9	Engineering
	Plutonium	(Pu)	99.99	Pilot
	Radium	(Ra)	99.9	Engineering
	Strontium	(Sr)	99.9-99.998	Pilot
	Thorium	(Th)	99.99	Engineering
	Uranium	(Th)	99.99	Engineering
	Zinc	(Zn)	90-99	Engineering

(a) Percentage of original amount remaining in the melt.

(b) Engineering-scale tests involve a melt depth of 1-2 ft. Pilot-scale tests involve a melt depth of 3-7 ft.

table should not be regarded as precise measurements of expected retention efficiencies. Table 4-2 also shows how metals can be divided based on tendency to volatilize.

4.2.1.1 Increasing the Retention of Metals

Retention of metals, if that is the treatment goal, may be increased by a number of mechanisms. These include:

- Reduction of generated gas
- Presence of a cold cap
- Recycling volatilized metals
- Decreasing melt temperature
- Modification of melt composition through additives

Reduction of Generated Gases. Gases evolved during vitrification can help carry metal particles and vapors to the surface. Greater gas evolution results in a more rapid movement to the surface, decreased exposure of the metals to the melt, and thus, decreased probability of the metals dissolving in the melt. Because the burning of combustibles during vitrification produces increased quantities of gas, gas-assisted movement of contaminants to the melt surface is one reason that combustibles are of concern during vitrification (see Chapter Seven).

Presence of a Cold Cap. Presence of a cold cap increases the contact-time between metals and the melt and thus increases the probability of metals dissolving in the melt.

In cold-top glass melters, metal vaporization has traditionally been solved by the creation of a "cold-top" layer or crust on the surface of the melt. This layer is formed by the incoming feed as it floats on the liquid melt, warms to melt temperature, and eventually dissolves into the melt. Because it is cooler than the melt, metals migrating to the melt surface may be trapped in the cold-top and sink back into the melt to be possibly incorporated into the glass.

ISV can be modified to increase metal retentions by implementing a similar mechanism. For example, in certain ISV applications, soil may be added above the melt to increase the amount of glass that has formed before contacting the contaminated layer. This increases the length of contact between the metals and the glass and increases the probability that the metals will be incorporated into the glass. Figure 4-1 illustrates the effect of melt depth on retention efficiencies for several metals.

Recycling Volatilized Metals. Metals that escape the treatment zone and enter the off-gas may be removed from the gas stream by the off-gas treatment system (typically removed by the scrubber solution). At this point, the contaminants may be considered for recovery, for recycling back to the molten glass to attain increased retention in the waste glass, or for separate disposal. Contaminants to be recycled may be removed from the off-gas system component, for example, by passing the scrubber solution through a filter aid and activated carbon. Contaminants can be returned to the melt to increase the overall immobilization efficiency of the vitrification treatment (Hansen, 1991). Contaminants to be recycled may also be recycled with the off-gas system component in which they were collected (e.g., by placing a contaminated high-efficiency particulate air (HEPA) filter directly into the melt) (USEPA, 1987).

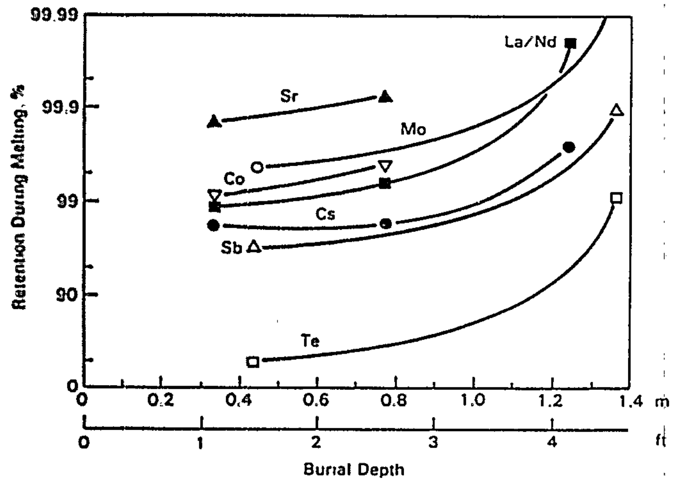

Figure 4-1. Element Retention Versus Burial Depth During Pilot-Scale ISV Tests (Buelt et al., 1987)

Decreasing Melt Temperature. An important processing variable which affects metal incorporation is melt temperature. Generally, the lower the temperature at which the melt proceeds, the lower the quantity of volatilized metals. This is apparently because the metals are incorporated into the molten glass before they volatilize (Hansen, 1991).

A primary factor controlling melt temperature is composition of the incoming feed. Feeds with high quantities of fluxing agents will melt at lower temperatures. This must be balanced against possible loss of product durability and the potential impact on other processing variables (Hansen, 1991; USEPA, 1989c).

For ISV, the development of the EFS may permit greater control over the rate of melt advance than previously indicated.

Modification of Melt Composition through Additives. The solubility of metals may be affected by changing the chemical composition of the melt. For example, reducing agents such as carbon and ferrous salts may reduce arsenates and selenates to lower valence compounds that are more volatile, thus reducing incorporation efficiencies of these metals (Schreiber et al., 1988).

4.2.1.2 Experience with Selected Metals

Following are selected treatment data for several metals.

Arsenic. Arsenic (As) is a semi-volatile metal which can be difficult to incorporate into waste glass. Vitrification has been evaluated as a BDAT by EPA for the following arsenic and selenium (chemically similar to arsenic) waste streams: D-004, D-010, K-031, K-084, K-101, K-102, P-010, P-011, P-012, P-036, P-038, P-103, P-114, P-204, P-205, and P-336 (Federal Register, 1991).

In general, waste glass containing arsenic exhibits reduced concentrations in the leachate for both Extraction Procedure Toxicity (EP Tox) and TCLP tests. Twidwell and Mehta (1985) found that glass made from slag containing arsenic in concentrations of 0.3 - 23.5 wt% showed 0.007 - 1.791 mg/L of As in the leachate (EP Tox). Chapman (USEPA 1990a) reported that waste glass composed of 17 mg/kg As showed <0.005 mg/L As in the leachate (EP Tox). Rhone-Poulenc (USEPA, 1990a) found that glass made from sludge containing arsenic sulfide in concentrations of 2.0 - 2.5 wt% showed 0.5 ppm (EP Tox) and <0.5 - 2.5 ppm (TCLP).

Arsenic is more volatile in some forms than in others. For example, arsenic oxide may be more volatile than calcium or iron arsenates. Certain waste feeds may require chemical or thermal pre-treatment to convert arsenic oxide to less volatile forms before vitrification (USEPA, 1990a). Twidwell and Mehta (1985) converted arsenic oxide (As_2O_3) in flue dust to a mixed calcium oxide ($Ca_3(AsO_4)_2$)via slow roasting. The calcined mixture was dissolved in a molten iron silicate slag at temperatures up to 1290°C. These results indicated that arsenic oxide, although volatile, may be successfully vitrified.

Cesium. Cesium (Cs) is also a semi-volatile metal. It is common at DOE waste sites in its radioactive isotope, ^{137}Cs. Due to its volatility and radioactivity, ^{137}Cs presents a difficult remediation challenge. Researchers have studied its behavior during vitrification in tests for a number of vitrification processes. Several of these tests are summarized below.

The volatilization of cesium and other semi-volatile radioactive metals has been a concern at several potential ISV sites, including ORNL (Spalding and Jacobs, 1989). This concern arises because volatilized cesium must be removed by the off-gas system, which increases the quantity of secondary contamination that must be handled. At ORNL, the treatment of a typical trench would require ten ISV settings, each of which would produce a quantity of waste. Therefore, despite retention efficiencies of 99.88% in pilot-scale tests, the total waste generated over the course of a trench clean-up was considered too high for remediation goals.

The initial method to minimize ^{137}Cs volatilization focused on adding sodium oxide (Na_2O) or sodium carbonate (Na_2CO_3) to the soil prior to melting (Spalding and Jacobs, 1989). This reduces the soil-melting temperature and Cs is captured in the melt before it can volatilize. However, bench-scale testing indicated that use of sodium as a flux increased gas evolution and caused additional amounts of ^{137}Cs to be carried to the surface. These two mechanisms balanced and the net result was no difference of ^{137}Cs incorporation in the melt, whether or not a flux was added. As a result, recent attempts to control cesium volatilization focus on use of the EFS to control processing characteristics and on recycling off-gases by placing a HEPA filter prior to off-gas entry into the off-gas system. The results of a second pilot-scale test indicated that these methods successfully curtailed generation of secondary off-gas system wastes.

Composition of the feed may also impact retention efficiencies for cesium. Early tests that prepared for use of vitrification at West Valley studied the ability of a LFCM to incorporate cesium. Those tests found that the predominate variable controlling cesium incorporation was the halogen concentration in the feed. Increased chlorine content in the feed decreased the incorporation of cesium in the glass. Air inleakage into the melter, plenum temperature, feed rate, and waste loading were the processing variables examined and found not to be important in cesium retention (Goles and Anderson, 1986).

Tests in Japan using a microwave vitrification process also found that feed composition influenced cesium retention. This research reported that the amount of volatilized cesium could be reduced by half by adding a flux of 20 wt% B_2O_3 to the feed. The B_2O_3 also reduced the leachability of the waste glass (Komatsu et al., 1990).

At the SRS, cesium volatilized during HLW vitrification is scrubbed from the off-gas with a 99.99999+% efficiency and recycled to the melter feed (Wicks and Bickford, 1989).

4.2.2 Non-Metallic Inorganic Contaminants

Non-metallic inorganics found in waste include, but are not limited to, cyanides, ammonia, various acids, asbestos, radon (a radioactive gas), halogens, and oxides of nitrogen, sulfur, and phosphorous. These inorganics are a concern because they may adversely impact processing.

These non-metallic inorganics react to vitrification in a variety of ways. This is because some are compounds, such as asbestos and cyanides, and some are elements, such as the halogens. Compounds such as cyanide and asbestos decompose to their constituent molecules and atoms and then follow the path typical of inorganics or organics, as identified in this or other sections of this chapter. Elements, such as halogens, form compounds of different types depending on melt conditions, feed composition, and other factors. In these various forms they may either incorporate into the glass, evolve as off-gases, or follow other applicable pathways.

The following sections address asbestos, radon, halogens, and important inorganic oxides. Other inorganics (such as cyanides and acids) will not be addressed since they are compounds that primarily decompose into constituents and description of their behavior will therefore be redundant. Asbestos will be described in greater detail than the other substances because it is a contaminant widely targeted for treatment by vitrification. Halogens and the addressed inorganic oxides are generally not the contaminants targeted for treatment by vitrification, but evolve as part of the treatment process and thus require attention.

4.2.2.1 Asbestos

Asbestos is a fibrous material composed of silicates, metals, and either water of hydration or hydroxides. For example, the chemical formula for crocidolite (blue asbestos) is $NaFe(SiO_3)\cdot FeSiO_3\cdot H_2O$. When subjected to temperatures of 400-900°C, water is driven off and the rest of the asbestos fibers are broken down to their constituent molecules or atoms. The constituents dissolve in the melt and are ultimately incorporated into the glass framework as the melt cools. Asbestos wastes are particularly amenable to treatment through vitrification because their high silicate content helps form part of the glass network (Roberts, 1989).

In order to successfully vitrify asbestos, the vitrification process must be capable of handling all the materials likely to have asbestos in them or to be mixed in with asbestos waste. These materials include paper, plastic, wood, concrete, brick, steel lath, copper, aluminum, rock wool, glass fiber, gypsum, plaster, clay, quartz, refractory material, and other materials (Roberts, 1989).

Destruction efficiencies of asbestos are primarily controlled by temperature and residence time in the furnace. In the Vitrifix process the furnace operates at 1300°C. At these temperatures destruction of asbestos takes 2-3 minutes. However, because asbestos is an insulator and a poor conductor of heat, residence time in the melter is 12 hours. Therefore, the probability of asbestos contact with the molten glass and its resulting destruction is greatly increased. Furthermore, the melter has a submerged throat which is not heated in any way. At temperatures less than 1100°C glass flow through the throat stops due to the increased viscosity of the glass. Glass exiting the furnace is thus ensured of exposure to temperatures in excess of those required for asbestos destruction (900°C or less).

The product of asbestos vitrification is a dark green to black silicate glass. Its physical properties are similar to those of container glass, but asbestos glass is more chemically resistant. Because this glass is produced from a waste stream with highly variable characteristics, it does not have the precisely controlled properties found in industrial glasses. However, it may possibly be used as a hard core, or in place of the ordinary glass found in sandpaper (Roberts, 1989).

Asbestos vitrification has been tested in both England and in the U.S. and the product reported free of asbestos fibers. In the Faslane site clean-up, a 5 ton/day furnace was used to remediate "hot-spot" soils contaminated with asbestos (Denner, Langridge, and Affleck, 1988). In 1987 at the Dalzeil Glassworks in New Martinsville, West Virginia, a proprietary asbestos process was demonstrated for the EPA. Results of this test showed safe handling of materials as well as an absence of asbestos in the waste glass. Air monitoring indicated that the process met Occupational Safety and Health Administration (OSHA) air quality standards for asbestos fibers, both inside and outside the materials handling area (Roberts, 1989).

Asbestos has also been incorporated in waste glass in bench-scale ISV melts (Farnsworth, Oma, and Bigelow, 1990).

4.2.2.2 Radon

Radon exists in rocks and soils and is spontaneously produced by radioactive decay. Because radon is a gas, it represents a difficult challenge to waste treatment processes. Vitrification is a potential option because the glass matrix severely limits the diffusion of gases (approaching no diffusion) with atomic radii greater then krypton (1.03 A) or xenon (1.24 A). Radon's radius is 1.343 A. Thus, the release of radon from the vitrified residues should be limited to that from externally exposed surfaces (Sing and Swallow, 1960). Pre-existing radon will be released during vitrification.

Results of bench-scale tests conducted on the Fernald K-65 residue indicated the potential of vitrification to effectively immobilize fission-product radon produced after vitrification. The non-vitrified K-65 residue tested "hazardous" by the EP Tox, and the radon emanation rate of 52,400 $pCi/m^2/s$ was over 2500 times the EPA limit of 20 $pCi/m^2/s$. After vitrification, the K-65 residue tested "nonhazardous" by the TCLP, and the radon emanation rate was 1.56 $pCi/m^2/s$ (Janke, Chapman, and Vogel, 1991).

4.2.2.3 Halogens

Halogens of primary concern are chlorine and fluorine. They are a concern because of their tendency to form compounds, such as dioxins, and because of the important ways in which they may affect vitrification processing.

Halogens exhibit low solubility in silicate glass and may be difficult to incorporate in the glass. However, this will vary with halogen and glass composition. Chloride exhibits a solubility of less than one percent, while fluoride has been incorporated into glass up to 9 wt%. Tests on wastes from the Weldon Spring site, Missouri, indicated that the glass produced from soils at that site would hold no more than 5 wt% fluoride. As the waste feed held more than 5 wt% fluoride (about 10 wt% fluoride), additives were required to dilute the fluoride and bring it within the solubility of the glass (Koegler, Oma, and Perez, 1988). Other reports have indicated volatilization of about 50% of the fluorides in the feed (Loewenstein, 1983).

Halogens may also enter the off-gas system. If chlorine enters the off-gas system as hydrochloric acid (HCl) gas, it can be removed by the spray chambers and transformed into salts such as NaCl, $CaCl_2$, or some other innocuous chemical. Fluorine in the off-gases may corrode the melter (Bonniaud et al., 1986).

4.2.2.4 Inorganic Oxides of Concern

Primary inorganic oxides of concern include nitrogen oxides (NO_X), sulfur oxides (SO_X), and phosphorous compounds (such as P_2O_5 or PO_4^{2-}).

NO_X and SO_X will exit the melt to the off-gas system and are regulated compounds. In general, nitrogen and sulfur do not exhibit high solubility in silicate glass (< 2%) and thus may necessitate treatment by the off-gas system. As NO_X and SO_X are common process emissions, off-gas systems designed to treat them are available. Chapter Six discusses off-gas treatment in greater depth.

Nitrogen, sulfur, and phosphorous oxides are also a concern because of the way in which they may influence processing. For example, P_2O_5 increases glass corrosiveness and glass viscosity. Both tendencies may increase the cost of vitrification, although by different mechanisms. Sulfur, on the other hand, may increase the tendency for the glass to foam, increase metal corrosiveness in the off-gas system, and form molten salts in the melt (Chapman, 1984). The decomposition of NO_3 may cause oxidizing conditions in the melter plenum and thereby may contribute to the volatilization of iodine and ruthenium (Smith, Nyman, and Anderson, 1990).

4.2.3 Organic Contaminants

The treatment of organics is, in one sense, a by-product of vitrification. This does not mean that vitrification is ineffective in treating organics. Organics, both contaminants and non-contaminants, are primarily destroyed thermally during vitrification. Tables 4-3 and 4-4 present organic DE's and DRE's for ISV and glass melters. Potential fates of organics include the following: (1) destruction via pyrolysis or combustion, (2) removal in the off-gas system, (3) migration to adjacent soil during the vitrification process.

Destruction of organics occurs primarily via pyrolysis in the melt and combustion in the plenum or in the secondary combustion chamber. Ideally, organics will degrade completely to form products such as carbon dioxide (CO_2), water, and HCl. Conditions in the plenum or combustion chamber may often be controlled to maximize the combustion of escaping organic products and the production of the desired off-gases. Those organics and organic by-products that still exist as contaminants are removed in the off-gas system.

As described previously, organics may be released during vitrification to the off-gas system or by migrating into the surrounding soil. One criticism of ISV is the possibility that organics may migrate into the surrounding soil. If this criticism is correct, ISV may potentially transform a small area of manageable contamination into a much larger area of contamination, even if a high percentage of organics are destroyed.

4.2.3.1 Increasing Destruction Efficiencies of Organics

Methods to increase DE's of organics include:

- Cold cap
- Secondary combustion chambers
- Recycling to melt

Cold Cap. The creation of a cold cap increases the length of time organics are exposed to the melt and thus also increases DE's via pyrolysis. As with metals, one potential method to increase organic DE's of ISV is to cover the site with a layer of clean soil. Engineering-scale ISV tests have shown that DE's for organics may increase from 97% (when the contaminated soil is not covered with a layer of clean soil) to greater than 99.99% when an uncontaminated layer of soil is placed over the contaminated site (Buelt, Timmerman, and Westsik, 1989).

Secondary Combustion Chambers. Control of conditions in a secondary combustion chamber or in the plenum may increase organic DE's. For example, in early tests, Retech's PCR produced unacceptable levels of carbon monoxide (CO). By increasing the quantity of oxygen (O_2) in the secondary combustion chamber, organics in the off-gases burned more completely and CO_2 was produced instead of CO (Eschenbach, Hill, and Sears, 1989).

Recycling to Melt. Finally, as with metals, organics that are not destroyed but that are captured in the off-gas system may be recycled to the melt to increase DE's. They may first be removed from the off-gas component which captured them or the organic contaminants may be recycled intact with the component.

Table 4-3. ISV Organic Destruction and Removal Efficiencies(*The Hazardous Waste Consultant*, 1990b)

Contaminant	Initial Concentration (ppb)	Percent Destruction	Total DRE (including off-gas removal)
Aldrin	113	>97	>99.99
Chlordane	535,000	99.95	>99.999
DDD,DDE,DDT	21-240,000	99.9-99.99	>99.999
Dieldrin	24,000	98-99.9	>99.99
Dioxins	>47,000	99.9-99.99	>99.9999
Fuel Oils	230-11,000	>99	>99.999
Furans	>9,400	99.9-99.99	>99.9999
Glycol	NA	>90	>99.99
Heptachlor	61	98.7	>99.99
MEK	NA	>99	>99.999
PCBs	19,400,000	99.9-99.99	>99.9999
Pentachlorophenol	>4,000,000	99.995	>99.99999
Toluene	203,000	99.996	>99.99999
Trichloroethane	106,000	99.995	>99.99999
Xylenes	3,533,000	99.998	>99.99999

Table 4-4. Demonstrated Organic Destruction Efficiencies for Vitrification Systems[1]

Compound	°C for 99% Destruction in 2 Seconds	Measured DE (%)
Hydrocyanic Acid	482-866	NA
Chlorobenzene	482-866	99.99986
Formic Acid	318-368	NA
Phosgene	427-479	NA
Methylene Chloride	427-479	>99.9995
Phenol	374-421	99.99992
Acetone	374-421	>99.9995
Isodrin	374-421	>99.9998
Ethanol	374-421	>99.9995
Mustard Gas	318-368	NA
Nitrogen Mustard	318-368	NA
Carbon Tetrachoride	318-368	99.99988
Aldrin	318-368	99.99994
Dieldrin	318-368	>99.9995
Sulfoxide	218-316	>99.99
Endrin	38-160	>99.998
Dithiane	182-213	>99.96
Sulfone	NA	>99.995
Xylenes	NA	99.99817
DIMP	NA	>99.8
DMMP	NA	>99.8
ACN	NA	99.99996
AN	NA	99.9994

[1] Data collected from Armstrong and Klingler, 1985; USATHMA, 1988; Klingler and Abellera, 1989.

4.2.3.2 Contaminant Migration During ISV Treatment

As mentioned, one important question concerning ISV is whether contaminants migrate into the adjacent soil during treatment. This question is examined in general fashion below via the presentation of key empirical studies and a theoretical model. This question may also need to be addressed for a specific site via bench- and pilot-scale tests prior to implementation of ISV at that site. While this question applies primarily to organics, some volatile and semi-volatile inorganics, such as mercury, may require consideration.

Empirical Data. Numerous tests have failed to demonstrate significant contaminant migration during ISV (Campbell and Buelt, 1990; Campbell, Timmerman, and Buelt, 1990; Farnsworth, Oma, and Bigelow, 1990; Landau Associates, 1991; Timmerman and Peterson, 1990). For example, an initial engineering-scale test was conducted to address the question of organic migration. The soils in this test were contaminated with 500 ppm of PCBs. Results indicated that process destruction of PCBs was slightly greater than 99.9%. After off-gas treatment, the system DRE was >99.9999%. Analysis of the vitrified block showed no residual PCBs; considering the processing temperature, the data are reasonable. The soil adjacent to the vitrified area was also examined for PCBs but only limited quantities were detected (a maximum of 0.7 ppm of PCBs). These data were interpreted to indicate that the soil vitrifies faster than the PCBs diffuse and that for this reason they are unlikely to migrate from the vitrification zone during processing (Buelt, Timmerman, and Westsik, 1989).

The movement of organic chemicals has also been examined through mass balance studies. A water mass-balance study indicated a net migration of water into the vitrification and off-gas treatment zone (Buelt, Timmerman, and Westsik, 1989). In this study, researchers estimated that 33,800 liters of water were in the soil. Negative pressure under the hood withdrew another 9,000 liters of water from outside air. The amount of water leaving through the stack was estimated to be 47,500 liters. From this latter figure, 5,100 liters was subtracted to account for the water lost from the scrub tank in the off-gas system. The final balance was equivalent to 42,800 liters of water prior to vitrification and 42,400 liters of water exiting the off-gas system. The indicated net migration of water into the vitrification and off-gas treatment zone suggested at least partial movement of organics toward the melt, rather than migration from the melt. Another ISV test was performed on arsenic and mercury contaminated sludges from the M-1 holding ponds at Rocky Flats, Colorado (Jacobson and Mears, 1991). A mass balance conducted for this test failed to account for 37.5% of the arsenic and 53% of the mercury originally in the test chamber.

Theoretical Model. In addition to the empirical data presented above, geochemical and soil chemistry mechanisms have been presented to identify possible contaminant behavior in soil adjacent to the melt. Presented below is a brief summary of a theoretical model of contaminant migration (Dragun, 1991).

Seven soil mechanisms impact contaminant migration during ISV:

- Concentration diffusion
- Gaseous convection
- Thermal diffusion
- Chemical reaction acceleration
- Pressure diffusion
- Capillary water migration
- Adsorption of water and chemicals onto soil particles surfaces.

Dragun argued that these mechanisms function differently in the five soil zones surrounding an ISV melt. Dragun hypothesized that, during ISV, the following soil zones form and remain in quasi-equilibrium: a melt zone (of molten glass), a pyrolysis zone (where organic destruction is initiated), a heat affected zone (where soil moisture is vaporized), a transition zone (where soil is heated from ambient temperatures to 100°C), and an ambient soil zone (of normal soil conditions).

After examining the mechanisms and the way in which they functioned in the five soil zones, Dragun argued that the net direction of organic contaminants would be toward the melt and ultimate destruction and not away from the melt to spread contamination.

CHAPTER FIVE

PRODUCT CHARACTERISTICS

The characteristics of the waste-glass that vitrification produces are among the primary reasons that this process is considered as a way of treating hazardous waste. This product is typically a dark-colored, glassy substance, but crystalline or non-vitrified material may also be present in the product.

This chapter describes the various components of waste glass durability, the volume reductions accompanying vitrification, and potential uses of the product glass.

5.1 Product Durability

Product durability is associated with important chemical and physical properties of waste glasses. These properties are closely interrelated and result from the structural characteristics of glass as described in Chapter Two. This section discusses these properties under three sub-sections: chemical immobilization, physical durability, and devitrification (i.e., the formation of a crystalline phase in a glass). In a fourth sub-section, estimations of waste glass's long-term stability are presented. Such estimations are important because the long-term durability of waste glass over geological time spans has not been directly measured.

5.1.1 Chemical Immobilization

The single most important characteristic of waste glass is chemical immobilization, or the ability of the waste glass to resist leaching of the immobilized contaminants when contacted by water or other liquids. Without this characteristic, the cost of vitrification is most likely not justified; similar destruction efficiencies may be achieved using other processes. Furthermore, it is because of the chemical durability of waste glass that it may potentially be used and re-used in a variety of applications.

Although everyday experience suggests that glasses are durable, all glasses do leach to some degree. For example, recent experiments with lead crystal have shown elevated lead concentrations of up to 21,530 μg/l in wine and brandy that was stored in lead crystal decanters from six months to five years (Graziano and Blum, 1991). This value is well above the maximum value of 50 μg/l allowed by EPA in drinking water. Additionally, elevated lead levels (mean of 68 μg/l) were identified within one hour in wine poured into lead crystal glasses. However, this does not address directly the leachability of waste glass: lead crystal contains 24-32 wt% lead oxide (PbO), significantly higher than values commonly found in waste glass.

The chemical durability of waste glasses has been evaluated for a wide variety of glasses, wastes, processing types, and storage conditions. In addition, tests have indicated that non-glassy by-products of vitrification (i.e. metal wastes and devitrified or crystalline wastes) may also demonstrate high contaminant immobilization.

Leach Tests of Waste Glasses. Waste glasses have been subjected to numerous leach tests. These tests include the 24-hr Soxhlet Leach Test, the 28-Day Materials Characterization Center Test (MCC-1), the EP Tox, the TCLP, and the method used by the International Atomic Energy Commission (IAEC) (Buelt et al., 1987; Komatsu et al., 1990). Results generally indicate leach rates below the levels set as acceptable by the EPA. Sample leach rates for selected metals are presented in Table 5-1. Based on the results of EP Tox and TCLP tests conducted thus far, it is likely that waste glass may be below regulatory levels under the provisions of these tests.

One cautionary note concerning leach rates: low leach values of the product do not necessarily indicate chemical immobilization; they may indicate failure to incorporate the metal of concern into the waste glass. For example, mercury may volatilize during vitrification and fail to be incorporated in the melt. If this happens, low leach values for mercury may be more indicative of the particular process's difficulty in incorporating mercury into glass than of a leach resistant glass. Therefore, for volatile contaminants, a mass-balance may need to be performed to fully address the chemical immobilization afforded by a particular glass.

The leach rate of ISV waste glass was compared with the

Table 5-1. TCLP Leach Data for Selected Processes and Selected Metals*

Metal	Glass Melter[1,a]	Kiln/Vitrification Process[2,b]	ISV Glass[2,c]	ISV Metal[2,c]	TCLP Limits[2]
Arsenic	<0.02	<0.01	<5	<5	5.0
Barium	<0.05	<0.175	0.05	<1	100.0
Cadmium	0.007	0.015	<1	<1	1.0
Chromium	0.03	0.825	<1	2.7	5.0
Lead	<0.05	0.15	<1	<1	5.0
Mercury	<0.0002	0.00035	<0.03	<0.03	0.2
Silver	<0.01	0.01	<0.1	<0.1	5.0

[1] in ppm
[2] in mg/l
[a] Penberthy Electromelt International, Inc., vendor information
[b] Harlow et al., 1989
[c] Farnsworth, Oma, and Bigelow, 1990.

* As original contaminant concentrations and process DRE's were not always supplied, this leach data is not directly comparable. This data is presented to show that, in general, vitrification products pass TCLP limits.

leach rate of other durable glasses using data from the Soxhlet Leach Test. Results indicated that the leach rate of the ISV waste glass is significantly less than that of marble or bottle glass and is comparable to Pyrex glass and granite (Buelt et al., 1987). Figure 5-1 presents this comparison.

Leach Tests of Non-glass Waste Forms. In addition to the leaching of waste glass, the leaching of non-glass waste forms has been studied. Non-glass waste forms produced during vitrification include crystalline material mixed in the product and the metal that may settle to the bottom of the melter or molten region.

Researchers at ORNL have compared the leaching of the crystalline-phase ISV product to the glass-phase ISV product. Results from a field demonstration indicated that every element tested, with the exception of Cs, was more extractable into 0.1 normal HCl from the crystalline phase than from the glass phase, but generally by a factor of less than 10. Although the absolute magnitude of the concentrations of the elements released by acidic extraction is not directly comparable with the release rates under environmental conditions, it does support the conclusion that most elements will be more susceptible to leaching from the crystalline phase than from the glass phase in these systems (Spalding and Jacobs, 1989). This conclusion is supported by research for both commercial and defense nuclear waste glass. Under most conditions, leachability can increase after samples are devitrified, but this increase is generally less than a factor of 10 (Wicks, 1985).

The metal product formed from the pooling of metal at the bottom of an ISV glass monolith has also been leach tested. The metal product from bench-scale tests on simulated wastes in Idaho National Engineering Laboratory (INEL) soils indicated that it would pass the TCLP. These tests included arsenic, barium, cadmium, chromium, and silver in the melt (Farnsworth, Oma, and Bigelow, 1990). The metal ingot formed from an engineering-scale test of ISV of a UST passed the EP Tox for the 8 metals tested: arsenic, barium, cadmium, chromium, lead, mercury, selenium, silver (Campbell, Timmerman, and Bonner, 1990).

Toxicity Tests of ISV Waste Product. EPA compared the leachability of chemically-stabilized soil and vitrified (ISV) soil in treatability studies for the Western Processing

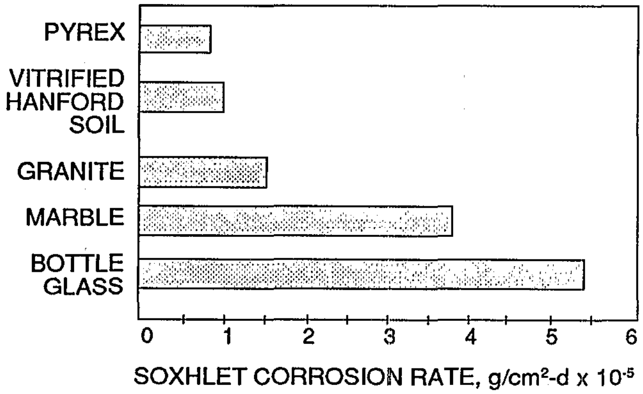

Figure 5-1. Leach Resistances of Selected Materials (Buelt et al., 1987)

Superfund Site. In this study, eluates were prepared from untreated soil, soil stabilized by three chemical stabilization processes, and vitrified soil. They were then compared for metal releases and toxicity effects on algae and an invertebrate. Results indicated that chemical stabilization increased toxicity to both organisms. In contrast, testing of the vitrified soil indicated that vitrification reduced toxicity to the algae, with no toxicity to the invertebrate. The researchers concluded that the stabilization techniques were inappropriate for the Western Processing Superfund Site, but that vitrification was appropriate (Green et al., 1988).

WIPP In Situ Testing Program. The durability of nuclear waste glasses over time in the storage repository is an important consideration in decisions concerning glass composition, packing materials, and container materials. The first in situ tests involving burial of simulated HLW forms conducted in the United States were started on July 22, 1986. These tests are being conducted at the Waste Isolation Pilot Plant (WIPP) near Carlsbad, New Mexico. This effort is known as the Materials Interface Interactions Tests (MIIT) and is international in scope. The MIIT program is a joint effort managed by Sandia National Laboratories in Albuquerque, New Mexico and the Savannah River Laboratory (SRL) in Aiken, South Carolina and sponsored by DOE. In the MIIT tests, multiple nonradioactive waste glass samples were placed in brine and salt in an underground test facility under conditions simulating those in a salt repository. Included in these tests were over 900 waste forms comprising 15 different systems supplied by 7 different countries. In addition to the waste glass samples, 300 potential canister (or overpack) metal specimens and 600 backfill and salt geologic samples are being tested (Wicks and Molecke, 1986; Wicks et al., 1990).

While the total program was scheduled to run 5 years, samples and aliquots of solution were removed and studied after 0.5, 1, and 2 years. Preliminary results indicated that the SRL waste glass system SRL 165/TDS performed well in the salt environment at WIPP and was not significantly affected by proposed canister or overpack metals. Leach data indicated that the rate of dissolution decreased with increasing time. In addition, selective leaching appeared to be the main leaching mechanism. The leaching process was characterized by the formation of two precipitate layers over three glass interaction zones that contribute to protecting the glass from further leaching with time. Additional results will correlate the results of the SRL system with differing glass systems of other countries and provide additional details on the leaching mechanisms involved (Wicks et al., 1990).

5.1.2 Physical Durability

Waste glasses produced by staged ISV and JHCM vitrification were compared for their compressive and tensile strengths and found to be very resistant to fracture into smaller pieces (Koegler et al., 1989). The waste for these tests came from the raffinate sludges at Weldon Springs, Missouri. These glasses were produced from predicted waste stream compositions given bench-scale test results, and their strength performances are presented in Table 5-2. Two formulations of ISV waste glass were tested based on alternative ISV implementation plans. As the data shows, the vitrification processes tested had similar strength characteristics. The compressive and tensile strength of concrete is included for comparison. From this comparison, it can be seen that the strengths of waste glasses range from 5 to 20 times that of concrete.

The impact resistance of partially devitrified and glassy waste glass systems was studied at various temperatures and impact velocities for both small and larger scale samples at PNL and SRS. Results indicated that for extreme-case scenarios simulating a high-speed train impact at 80 mph, the fracture of glass was localized to the area of impact. Furthermore, the surface area of the glass in the canisters was limited to an increase of about a factor of 40. No major differences were observed between small and large samples, nor between glassy and partially devitrified products. Finally, the amount of particles smaller than 10 µm produced after impact was small. Minimizing the production of particles of this size is important because they are potentially dispersible via air currents (Wicks, 1985).

Table 5-2. Strength Comparisons of Waste Glasses Produced by ISV and a JHCM (Koegler et al., 1989)

Source of Waste Glass	Compressive Strength (psi)	Tensile Strength (psi)
ISV (50% sludge/50% soil)	59,350	4,410
ISV (20% sludge/10% soil/70% liner)	43,210	4,309
JHCM	43,210	4,300
Unreinforced Concrete	3,000 - 8,000	400 - 600

Impact resistance studies were also conducted at Argonne National Laboratory for impact energies up to 10 J/cm^3. The amount of dispersible fines produced was very similar to the amount of fines produced after impacting common industrial glasses such as Pyrex (Wicks, 1985).

5.1.3 Devitrification

Devitrification is the formation of a non-glassy, crystalline structure in the waste product. Devitrification may occur during cooling of the molten glass. Devitrification may also occur after the glass has cooled if, for some reason, the amorphous glass structure crystallizes. The degree of crystallinity and crystalline phases that may be produced depend on factors such as the specific cooling rates, sizes of the forms, and the physical and chemical composition of the waste-glass.

Assuming that the melt has a chemical composition appropriate for glass formation, devitrification during cooling may be caused by slow cooling and subsequent nucleation growth. Slow cooling increases the likelihood that a crystalline structure can form before the amorphous structure "freezes." Fast cooling minimizes devitrification by "freezing" the amorphous structure of the molten glass into a solid. As a result, because large ISV melts cool more slowly, they may have higher concentrations of crystalline structure than monoliths arising from smaller melts. Furthermore, devitrification will most likely occur in the center of the waste glass due to slower heat losses there (Means et al., 1987; Jantzen and Bickford, 1985). Rapid cooling of the molten glass past the annealing range may reduce devitrification quantities in wastes where this is a concern (Wicks, 1985, 1986).

If reheated, glass may also devitrify after it has hardened. This is particularly a concern for nuclear glasses, as the radioactive decay process may generate additional heat in the glass. Temperatures in the waste glass may be reduced by adding less radioactive waste to the glass or by using aged waste. However, the storage temperature of defense waste glass will generally be less than 100°C, and devitrification occurs at temperatures above 500° C. Furthermore, as indicated above, even if devitrification increases waste glass leaching, data indicates this will still be at acceptable levels (Wicks, 1985).

5.1.4 Estimation of Long-Term Durability

Because the long-term durability of waste glasses has not been directly measured, estimates of long-term durability are very important. Natural glasses, such as obsidian and basalt, and durable synthetic glasses, such as Roman glasses, give some idea of the potential durability of waste glasses. However, there is a wide range in their measured durability, from millions of years for the natural glasses to the several centuries demonstrated so far for the synthetic glasses. Furthermore, the fact that glasses in general may last a long time does not mean that a particular waste glass will last as long. Nor does it permit quantitative predictions of the expected durability of the specific waste glass (Jantzen, 1988).

To address these concerns, two different methods have been used to predict waste glass performance: kinetic models and thermodynamic models. Kinetic models mathematically describe the processes that affect the leaching behavior of a glass: ion exchange, diffusion, and the formation of protective layers. Kinetic models describe the leaching behavior of a glass over time and indicate that waste glasses should be very durable. Some of the components of a kinetic model are described in Chapter Two. However, kinetic models cannot identify which of several glasses is predicted to be most durable (Jantzen, 1988; Wicks, 1985).

The thermodynamic approach is based on the work of Newton and Paul (1980). They found a logarithmic relationship between the free energy of hydration of glasses and measures of reaction progress, such as K_2O release from the glass, and "loss of thickness" of a glass, measured in millimeters lost per century (Jantzen, 1988). The free energy of hydration of a glass is estimated by summing the known free energies of hydration of the oxides, such as SiO_2, which compose it. This summed value can then be compared with the free energy of hydration of glasses known to be durable. Using this method, the durability of the most durable nuclear waste glasses was estimated to be comparable to that of natural glasses millions of years old. The durability of the least durable nuclear waste glasses was estimated to be similar to that of Medieval glasses with an expected favorable durability of at least 1,000 years (Jantzen, 1988).

The thermodynamic model has been used to develop the quality assurance plan for the production of nuclear glasses at the DWPF at the SRS. By estimating the free energy of hydration of the incoming feed prior to vitrification, an estimate of the quality of the waste glass can be made. This is done by comparing the free energy of hydration of the feed with the hydration free energy of the benchmark glass used in the National Environmental Policy Act (NEPA) process for the DWPF (USDOE, 1982). If this comparison indicates that the feed will produce a low-quality waste glass, it is modified to improve expected performance. This comparison is carefully evaluated using a statistical system designed to account for variability in sampling, analyses, processing, and free energy/waste glass durability relationships (Postles and Brown, 1992).

The long-term durability of ISV glass has also been calculated. This was accomplished by estimating the leaching behavior of ISV for a 1,000-year period based on the leach results of the MCC-1 test. These results were then compared with the leaching of obsidian over 1,000 years. Given the similarity in leaching behavior over 1,000 years, and given the structural similarity of ISV glass and obsidian, the ISV glass was estimated to have a durability similar to obsidian, on the order of 1,000,000 years (FitzPatrick, 1986; Buelt et al., 1987).

5.2 Product Volume Reductions and Densities

During vitrification, the incoming waste is generally reduced in volume and increased in density. This reduction in volume is the result of the vaporization of void gases, the vaporization of water in the feed, and the combustion of organic materials present in the feed.

Volume reductions include: 25-45% for ISV; 70 - 80% for glass melter vitrification of incinerator ashes; 90% for glass melter vitrification of asbestos wastes; and 98-99.5% for microwave melter vitrification of liquid and sludge wastes. Obviously, volume reduction values will vary widely with waste feed. As water is vaporized and organic components are destroyed, waste feeds with high moisture contents and/or high organic content will likely have greater volume reductions than those without. The volume reduction during an ISV melt results in a depression at the treatment site which may be filled with clean soil or other fill.

The density of vitrified products ranges from 2.3 to 3.0 g/cm^3. The ISV product has been measured at 2.3 to 2.65 g/cm^3 (Buelt et al., 1987), while ex situ vitrification products have been measured at 2.7 to 3.0 g/cm^3 (Komatsu et al., 1990). Differences in the densities appear to be due to the increased control which operators have over the ex situ methods. However, all values are well above the densities of 0.7-2.2 g/cm^3 measured for stabilized/solidified products (Stegman, Cote, and Hannak, 1988).

5.3 Product Use

Potential uses for melter glass include aggregate, glass wool, and other ceramic products. In general, given the variation present in most waste streams, making a consistent, sophisticated glass product from waste glass may prove difficult (Roberts, 1989).

Depending on how the molten glass is treated, different products may be formed from the product. If the molten slag is poured into water, the glass shatters as it cools and a glass frit is formed. This frit may possibly be used as is for aggregate in road building, or for abrasive materials such as sandpaper, shot blast, or grinding media (GRI, 1989; *The Hazardous Waste Consultant*, 1990a). The size of aggregate pellets may be controlled by varying the speed of the screw conveyor into which the molten glass is poured (Harlow et al., 1989).

If the molten glass is spun as it cools, glass fibers will be formed which can be used as mineral wool or glass wool for insulation or in other ways (Vaux, 1988; Hnat et al., 1990a).

Potentially, the waste glass may also be molded or reformed and used in the production of architectural materials (such as wall and floor tiles, patio stones, mosaics, sinks, tubs, and countertops) or refractory materials (such as high-temperature bricks and other insulating materials) (Roberts, 1989; *The Hazardous Waste Consultant*, 1990a).

The ISV monolith has several potential uses, including building foundations and subsurface barriers. Subsurface barriers would prevent groundwater and biological organisms from moving into or out of the contaminated area. Thus, the contaminants would be isolated from the ecosystem and the site spared the need for further treatment (Shelley, 1990; Buelt et al., 1987).

CHAPTER SIX

OFF-GAS TREATMENT

Off-gases from the melt may contain volatilized metals and other inorganics, undestroyed organics, by-products from the pyrolysis of organics, and other chemicals of concern. Discussion of off-gases addresses three areas in this chapter: potential off-gases of concern, potential impacts of off-gas constituents, and potential controls aimed at minimizing undesired off-gases.

6.1 Off-Gas Components

Off-gases are composed of inleakage air, water vapor, chemical decomposition products (e.g., CO_2, H_2O, and HCl), and entrained particulates, as well as volatilized inorganics.

Inleakage air comes from leaks in the melter that permit air to move into the melter. The primary source of inleakage air is the air that enters the furnace with the feed material. Other factors, such as age of the equipment, may also contribute to leaks. Inleakage air is a concern because it may create convection currents in the plenum that may entrain particles and contaminants from the cold crust. These particles complicate off-gas treatment (Holton et al., 1988).

Water is vaporized in the plenum by contact with the melt as the feed is rapidly heated by the high temperatures there.

Depending on the feed material, the products of decomposition may form a significant component of the off-gas system. Feed material with high quantities of combustibles, concrete, and/or other gas-producing materials may produce significant amounts of gas in the melt (Buelt et al., 1987). The significance of these gases is that they may form an important pathway for the movement of inorganics out of the melt (carrier gas transport). Therefore, high quantities of gas-producing materials may result in the need for an effective off-gas system.

Entrained particles may be produced from the feed dust (Koegler et al., 1989). They also may be produced at the high temperatures of vitrification from volatile glass components (Bonnioud et al., 1986). Again, these may serve as carriers for a variety of contaminants such as inorganics and PCBs (Battey and Harrsen, 1987). Entrained losses represent a physical loss mechanism (Goles and Anderson, 1987).

Volatilized inorganics are a concern because they are often represented by the contaminants that are sought to be controlled. The difficulty in incorporating these in the melt has already been described (Chapter Four) and will not be repeated here.

6.2 Constituents of Concern

Classes of constituents that are commonly controlled during vitrification include the following:

- metals - volatile and semi-volatile
- organics
- particulates
- sulfates and sulfur oxides (SO_x)
- nitrogen compounds (NO_x)
- carbon monoxide (CO)
- hydrogen halides and halogens

These compounds are of concern for a variety of reasons. Metals and organics represent the very contaminants which treatment by vitrification is attempting to control. Particulates function as an important pathway in carrying contaminants from the melt and through the off-gas system. Sulfates and sulfur oxides, nitrogen compounds, and CO may be produced during the vitrification process and represent air pollutants which must be controlled. These compounds also may cause corrosion of the melter. CO is characteristic of incomplete combustion and may indicate that greater processing controls need to be exercised in the plenum or secondary combustion chamber. Halogens such as flourine and chlorine are difficult to incorporate into the melt and may also corrode the melter if they evolve as off-gases.

6.3 Means of Off-Gas Control

There are a number of methods available to control off-gas emissions. These may be broken down into two strategies: reduction of emissions to the off-gas system, and treatment of evolved off-gases. These strategies can be grouped as follows:

Reduction of emissions:

- modification of the feed
- presence of a cold cap
- control of the environment in the secondary combustion chambers
- recycling of contaminants captured in the off-gas system

Treatment of evolved off-gases:

- operating with negative pressure
- design of the off-gas treatment systems

6.3.1 Reduction of Off-Gases to Off-Gas System

Reduction of off-gases forms an important means of off-gas control. Numerous methods permit control of off-gases at the source of production.

<u>Modification of the Feed</u>. Feed modifications may include adding materials to or removing materials from the waste before melting. For example, fluxes may reduce volatilization of inorganics by permitting melting at lower temperatures. Melting at lower temperatures decreases the percentage of particles that receive enough energy to volatilize. These particles may then be removed as the glass is tapped before they volatilize. However, addition of fluxes may change the character of the melt and increase volatilization in other ways. For example, bench-scale test for ISV application showed that sodium carbonate additions reduced melt temperature, but caused no net decrease in cesium volatilization because increased gas evolution resulted in increased cesium entrainment (Spalding and Jacobs, 1989).

Modification of feed may also change the chemistry of the melt and potentially increase retention efficiencies. For example, research has indicated that high mercury concentrations and/or high halogen contents may increase cesium volatilization, although by different mechanisms (Goles and Anderson, 1986). Reducing agents such as carbon and ferrous salts may reduce arsenates and selenates to lower valence compounds that are more volatile, and thus reduce incorporation efficiencies of these metals (Schreiber, 1988). If possible, constituents that decrease incorporation may be removed, or, at least, not added.

<u>Presence of a Cold Cap</u>. The cold cap helps minimize the volatilization of contaminants because it holds them in contact with the melt until they dissolve or decompose. As mentioned in Chapter Four, studies done with ISV have shown that increased cap widths over the molten soil increase metal retention.

<u>Control of the Environment in the Secondary Combustion Chambers</u>. Combustion of non-pyrolyzed organics and pyrolysis by-products occurs in the plenum or in the secondary combustion chamber. Control of conditions in these locations helps ensure complete combustion and thus reduces CO emissions and other products of incomplete combustion. One common method of modifying the combustion environment is to increase the flow of air or oxygen to these locations, ensuring the presence of adequate oxygen supplies for the combustion of all combustibles.

<u>Recycling of Contaminants Captured in the Off-Gas System</u>. A number of methods exist to recycle off-gas constituents to the melt. In one sense, these could be considered a treatment method for off-gases produced, because most recycling methods involve capturing the constituent of concern in the off-gas and then returning it to the melt. However, in this chapter recycling will be considered a type of off-gas reduction method, because it reduces total emissions of a particular off-gas constituent by increasing retention efficiencies.

The cold cap ("cold" relative to melt temperatures) is a first line of recycling. Here, volatilized contaminants and other materials may condense and fall back into the melt, thus increasing retention efficiencies. This method has been used in the glass melting industry to avoid losses of expensive materials, but also has potential for waste treatment.

Contaminants that leave the melt chamber and enter the off-gas system may be recycled after they are captured in the off-gas system. Captured contaminants may be recycled by removal from the off-gas system component in which they were captured (e.g., by passing the scrubber solution through a filter aid and activated carbon) (Hansen, 1991), or by placing the off-gas system component in which they were collected directly into the melt (e.g., a contaminated HEPA filter). This form of recycling the off-gases is a very powerful tool for increasing retention efficiencies. Repeated recycling of off-gases may eventually drive retention efficiencies close to complete incorporation. However, repeated recycling may also increase processing complexity, total treatment time, and costs.

All vitrification processes are amenable to recycling in some way or another. Ex situ processes may be more flexible to recycling options. However, ISV is also amenable to recycling. For example, at the 1991 ORNL pilot-scale test, a HEPA filter was placed at the junction of the hood and the ductwork carrying off-gases to the off-gas system. This HEPA filter reduced Cs emissions to the off-gas system and simplified off-gas treatment (Spalding et al., 1991). This filter could potentially be dropped into the melt close to power termination. Recycling may also be achieved at a subsequent ISV melt by placing secondary wastes from the previous melt into the soil at the second site before starting the melt. For example, pulsed periodic backflow through the HEPA filter could be used to flush contaminants from the filter. The flushed particulates could be dropped directly into the melt, or they could be deposited in a shielded container and buried at the next ISV site. The filter itself could also be unloaded, placed in a shielded container, and buried at the next ISV site.

6.3.2 Treatment of Evolved Off-Gases

Contaminants that have entered the off-gas stream will need to be removed. These contaminants may be recycled as described above, or disposed of as secondary wastes. If the contaminants contain valuable metals (such as mercury), they may possibly be recovered and sold. This section is concerned only with ensuring that gases in the off-gas system do not enter the environment before contaminants have been removed.

Operating with Negative Pressure. Operating the entire process at negative pressure is the first step for ensuring that contaminants do not enter the atmosphere. However, treating wastes with high amounts of organic wastes may produce enough gases to overwhelm the negative pressure in the off-gas system.

Two intermediate field tests of ISV were conducted at INEL in the summer of 1990 to examine the applicability of ISV to buried waste, potentially a major source of combustibles (Callow, Thompson, and Weidner, 1991). For these tests, pits were dug and filled with drums and boxes to simulate waste burial sites at INEL.

In the first of these tests, gas releases from containers resulted in 14 separate events, characterized by sharp temperature increases and/or pressure spikes in the hood. The pressure spikes were the result of either relatively slow gas releases from the melt, or relatively slow expansions of gases in the hood that occurred over a 10- to 30-second period. The pressure spikes were not rapid and therefore not characteristic of an explosive reaction. The intermediate-scale ISV system was unable to contain transient pressure spikes on several occasions. In cases where the pressure did not exceed 1 in. of water, the gasses were contained within the surge volume of the hood and subsequently drawn out to the off-gas treatment systems. When the pressure exceeded 1 in. of water, the hood was able to handle the pressure spike by relieving a portion of the excess gas through the HEPA-filtered pressure relief system. In extreme cases, when the pressure significantly exceeded 1 in. of water, the gas overcame the surge and pressure relief capacity of the hood and was released through any available point, including the base of the hood and through unsealed panel seams.

In the second intermediate field test, overburden was placed over the melt and the electrodes and EFS were slightly modified. These changes reduced the strength of the transient pressure spikes and the second test successfully avoided the problems associated with the first test.

Design of the Off-Gas Treatment System. Off-gas systems may remove particulates, recover heat and cool off-gases, neutralize acid gas, and remove water vapor. Components used to achieve these objectives include scrubbers, filters, spray chambers, spray channels, baghouses, and others. The off-gas systems of selected vitrification processes are presented in Table 6-1. Table 6-1 does not evaluate the efficiency of selected processes; it simply represents off-gas systems used in vitrification. Depending on site conditions and treatment goals, selection of an off-gas system may vary.

One concern of efficient off-gas treatment is the location of secondary waste in the off-gas system. The result of an ISV pilot-scale radioactive test will give some idea of how contaminants may behave in the off-gas system. This test was performed on transuranic-contaminated soil from a storage crib at Hanford (Timmerman and Oma, 1984). In addition to the transuranic contaminants, mixed fission products of ^{137}Cs, ^{106}Ru, ^{90}Sr, and ^{60}Co were added to the contaminated soil in order to study their behavior during an ISV melt. Table 6-2 presents the distribution of the material released from the melt to the off-gas system. While a small fraction of the off-gas fission products (3%) reached the primary HEPA filter, there were no fission products on the second-stage HEPA filter or in the stack samples taken downstream of the filters. The scrubbers accounted for removal of 65% to 92% of the radionuclides released to the off-gas, as indicated by the distribution of the radionuclides in the two scrub solutions.

Results from previous non-radioactive tests had indicated that the average mass-mean diameter of particles exiting the ISV hood was 0.7 μm, while the scrubbing efficiency of venturi scrubbers dropped off for particles smaller than about 0.5 μm. Given these characteristics of the off-gas system in the pilot-scale radioactive test, certain hypotheses concerning contaminant behavior as an off-gas could be made. First, the elevated distribution of cesium and ruthenium between the venturi and hydrosonic scrub solutions indicates that more of these volatile radionuclides were being released as very small particles. The distribution of cobalt indicates that these particles were also very small. Secondly, the transuranic elements were collected primarily in the venturi scrub solution, indicating that these elements were released as larger particles. Possible release of the transuranics as larger particles indicates that release of the transuranics may have been increased by the combustion of the test package containing the contaminated soil and fission products. This hypothesis is also consistent with the time that the transuranic levels started to increase in the scrub solution.

An important concern in waste treatment via ISV is secondary contamination. A pilot-scale ISV test revealed the location of the secondary contamination upon completion of the melt. In this test less than 1% of the radionuclides that escaped the melt settled on the ground. Less than 20% were deposited on the hood and off-gas piping. The 20% figure was for cobalt. The other nuclides were all less than 10%.

Contamination on the ground can be fixed in place before moving the hood and can be pushed into the subsidence zone when backfill is added. Deposits on the hood and off-gas piping can be fixed in place by spraying strippable fixatives so that the hood and off-gas line can be moved without concern for loose contamination. The fixative will then combust during subsequent operations. Spraying techniques for these procedures have been demonstrated with both pilot- and large-scale systems.

ISV was field demonstrated on a simulated radioactive liquid waste disposal trench at ORNL in July, 1987

Table 6-1. Off-Gas Systems for Selected Processes

Process	Off-Gas Component	Function
kiln[1]	oxidizer (three in series) semi-dry caustic scrubber fabric filter baghouses	combust organics neutralize acid gases remove dust and particulate
glass melter[2]	ceramic fiber filters gas-to-water heat exchanger water spray chambers (two in series) demisting chamber heater charcoal and HEPA filters	remove particulate cool gases neutralize acid gases remove water droplets re-heat gases above dewpoint filter remaining particles
ISV[3]	HEPA filter (optional) scrubbers (two in series) condenser heater HEPA filters (two in series)	initial filtering depending on treatment goals cool gases and remove particulate remove water vapor re-heat gases above dewpoint filter remaining particles
coal-fired vitrification furnace[4]	recuperator quench water precipitators and stack assemblies	recover heat cool gases remove particulate

[1] Harlow et al., 1989
[2] Freeman, 1986
[3] Battey and Harrsen, 1987
[4] Hnat et al., 1990a

Table 6-2. Radionuclide Distribution in the Off-Gas System During an ISV Pilot-Scale Test (Timmerman and Oma, 1984)

	Percent (%) of Total Radionuclides Released to Off-Gas						
						HEPA Filters	
Nuclide	Ground Surface[1]	Hood	Piping	Tank 1	Tank 2	Stage 1	Stage 2
Pu-239	0.09	4	<1	92	3	1	0
Co-60	0.05	4	14	24	55	3	0
Sr-90	0.05	4	<1	91	5	0.1	0
Ru-106	0.3	8	2	21	66	3	0
Cs-137	0.2	2	5	17	73	3	0

[1] Currently, a non-combustible fabric is placed as a ground cover inside the hood to prevent surface contamination.

Table 6-3. Hypothetical Distribution of ^{137}Cs Activity in ISV Off-Gas System After Vitrifying 10,000 Ci (Spalding and Jacobs, 1989)

Off-Gas System Component	Amount of ^{137}Cs (Ci)	Amount per Unit Area
Hood	0.079	0.24 µCi/cm^2
Ducting	0.401	5.5 µCi/cm^2
Scrub Solutions	11.74	0.5 µCi/mL
Primary HEPA Filter	0.293	1.46 µCi/cm^2
Secondary HEPA Filter	0.0008	0.04 µCi/cm^2

(Spalding and Jacobs, 1989). At this test, samples were taken at various points in the off-gas treatment system to determine what was happening to ^{137}Cs that was not incorporated into the melt. Based on the results of this test, hypothesized results for the treatment of a trench requiring 10 ISV settings is presented in Table 6-3.

While retention efficiencies for ^{137}Cs were measured at 99.88%, the amount to be treated by the off-gas system would generate significant secondary wastes over the course of treatment for an entire trench. Therefore, ways to reduce release to the off-gas system were examined. One recommendation involved placing a HEPA filter that would filter off-gas before it entered the system. This HEPA filter would thus filter incoming air and minimize entry of contaminants to the off-gas system and generation of secondary wastes. A pilot-scale ISV test at ORNL in May, 1991, indicated that a pre-filter successfully captured ^{137}Cs from the off-gases before they entered the wet scrubbing system (Spalding et al., 1991).

CHAPTER SEVEN

CAPABILITIES AND LIMITATIONS

This chapter describes the capabilities/advantages and limitations of vitrification that have been identified in the literature. As always, for specific site conditions, processing goals, and vitrification processes, these factors may or may not apply.

7.1 Capabilities

Potential capabilities and advantages of vitrification include:

- Thermal destruction of organics
- Reduced leachability of immobilized inorganics
- Long-term durability of the product
- Application to a wide variety of waste streams
- Application to a wide variety of contaminants
- Volume reduction
- Potential re-use of product
- Avoidance of excavation, processing, and reburial of product (ISV).

The first four of these capabilities are the direct result of the product. Capabilities five and six are the result of the flexibility of glass and the high temperatures under which vitrification is conducted. The last two capabilities are highly site-specific and will depend on site characteristics and treatment objectives.

Thermal Destruction of Organics. As described in Chapter Four, organics may be destroyed by pyrolysis and combustion during vitrification.

Reduced Leachability of Immobilized Inorganics. As Chapter Five pointed out, waste glasses of many types have shown reduced leachability of inorganics.

Long-term Durability of the Product. Long-term durability indicates a product that reduces leaching for long periods of time. It is possible to have a material that currently reduces leaching but that may not perform well over many years. Although not measured directly, the long-term durability of waste glass appears to be excellent and may extend to geologic time periods, as indicated by natural glass systems that have been stable for millions of years.

Application to a Wide Variety of Waste Streams. A representation of the waste streams to which vitrification may apply has been presented in Chapter Four. These will not be re-listed, but a review of that chapter will reveal that vitrification is potentially applicable to a wide variety of waste streams.

Application to a Wide Variety of Contaminants. Because vitrification is both a high temperature process and an immobilization process, it can apply to both organics (thermal destruction) and inorganics (immobilization). Vitrification may, therefore, be preferred at sites that present a complex mixture of hazardous and/or radioactive contaminants.

Volume Reduction. Not only does vitrification produce a long-term, chemically durable product, but it can reduce waste volume during processing. Thus, vitrification simplifies waste management.

Potential Re-use of Product. As described in Chapter Five, vitrified waste glass may potentially be re-used in various ways. Re-use may depend upon whether the product can be delisted according to EPA regulations and on whether the public will accept re-use of a product formed from hazardous wastes.

Avoidance of Excavation, Processing, and Reburial of Product. This applies only to ISV and may be important in two respect: worker safety and costs. If the site being remediated is highly contaminated, worker safety may be an over-riding concern. Potential worker contamination is minimized with ISV because contaminants are not brought to the surface. Costs may also be reduced by ISV because it avoids the costs of excavation, material handling, and disposal. If ISV is to be applied in staged application it will lose some of the in situ benefits.

Conversely, when compared with ISV, ex situ vitrification processes permit greater control over processing parameters. Included in control over processing parameters would be greater ease of feed modification, greater control of melt parameters, greater control of product characteristics, and greater control of organic combustion and offgas treatment. The trade-off in capabilities and disadvantages between ISV and ex situ vitrification processes are similar to those that exist in general between in situ and ex situ processes. Their relative importance will depend to a large extent on site conditions and treatment goals.

7.2 Limitations

The following may limit the effectiveness of vitrification:

- Feed moisture content
- Feed material composition
- Feed compatibility
- Presence of combustible material
- Presence of process-limiting materials
- Potential volatilization of contaminants
- Potential shorting caused by metals
- High cost of energy
- High cost of trained operators
- Depth limitations (ISV).

Feed Moisture Content. Feed moisture content has important impacts on vitrification economics, but in itself may not technically limit vitrification applicability. Vitrification may potentially drive off water during treatment, but in so doing requires more time, more energy, and, thus, drives up costs.

Limits of moisture content will depend on the process, but limits of 25 wt% and 20 wt% have been identified for some ISV processes (USEPA, 1987; USEPA, 1988). It is also possible that at greater than 5% free water, the water may react vigorously with the melt as it rapidly vaporizes (USEPA, 1990a). However, the DWPF has a much higher moisture content (>50 wt%) without a violent reaction occurring. One alternative to increase process ability to handle feeds with high moisture contents is to use heaters in the plenum. Plenum heaters may increase the speed with which water is vaporized and thereby the incorporation of feed material into the melt. By increasing incorporation speed in this way, treatment time and costs will be lowered.

ISV also may be able to drive off high concentrations of water. Most important in limiting ISV in areas of high moisture is soil permeability. As a general rule, soils having low permeabilities do not inhibit the ISV process, even in the water table, because the recharge rate is not significant in terms of the processing rate. The ISV melt advances at about 7 to 15 cm/h and soils with permeabilities of 10^{-5} cm/s or lower are thus considered to be vitrifiable, even in the presence of ground water or in the water table. Soils with permeabilities of 10^{-5} to 10^{-4} cm/s are considered marginally vitrifiable. Soils with permeabilities higher than 10^{-4} cm/s may require additional steps, such as drawing the local water table down by pumping and/or installing underground barriers, prior to ISV (Buelt et al., 1987).

Feed Material Composition. Feed material composition is defined here as the chemical composition of the material that is fed into the furnace or melter. As addressed in Chapters Two and Five, feed composition may impact the ability of the vitrification process to form a durable product.

Ex situ processes have an advantage in treating feeds with difficult compositions because additives can more easily be added to address feed difficulties. For example, IRI prepares its feed in batches. Samples of an incoming batch are taken and additives varied according to kiln requirements before the batch is fed to the kiln for processing (*The Hazardous Waste Consultant,* 1990a).

Potential problems resulting from difficult feed compositions are compounded with HLW because of the very hazardous (radioactive) nature of the waste. In many other vitrification applications, glass of poor quality may be remelted and reformed to improve quality. However, because of the hazard of HLW, the product glass cannot be re-melted once it is made. For this reason, the remediation process at SRS has included the development of the statistics-based quality assurance program described in Chapter Five.

For application of ISV, soils should contain adequate quantities of glass-forming materials (i.e., SiO_2 and Al_2O_3) and fluxes (i.e., Na_2O, K_2O, and CaO). The glass forming compounds in the soil provide the elements which form the skeleton of the amorphous glass product. Higher levels of these materials tend to increase the chemical durability of the resulting glass, but have the negative effects of increasing its viscosity and decreasing its electrical conductivity (Buelt et al., 1987). The flux agents are all alkali elements, such as sodium and potassium, that carry the charge that conducts the electric current generating the soil-melting heat during the ISV process. Therefore, soils with low alkaline contents may be unable to effectively carry a charge and thereby diminish the applicability of ISV (Campbell and Buelt, 1990). The minimum combined alkali concentration determined to be necessary for vitrification of soils using ISV has been variously identified as 1.4 wt% (Buelt et al., 1987) and 5 wt% (Lominac, Edwards, and Timmerman, 1989).

Two sites considered for ISV have soils which proved difficult for ISV to vitrify because of soil composition: Arnold Engineering Development Center (AEDC), Tullahoma, Tennessee and SRS, Aiken, South Carolina. Table 7-1 compares the compositions of 2 easily vitrifiable soils with soils from AEDC and SRS.

Bench-scale tests with soils from the AEDC site indicated problems vitrifying a soil which contained only 1% alkali elements. A flux of 5 wt% to 10 wt% sodium carbonate was judged necessary to vitrify the AEDC soil (Timmerman, 1989). The pilot-scale test added 27 wt% sodium carbonate to the top three feet of cover soil. Results indicated that the addition of flux would permit vitrification of AEDC soil. However, failure to reach target depths (the melt reached 5 ft.) indicated that treatment would require injection of the flux agent, rather than just surface placement, and thus some disruption of contaminated material would be required (Timmerman and Peterson, 1990).

Bench-scale tests were conducted on SRS soils having alkali elements (Na_2O and K_2O) of less than 0.2% wt. These tests evaluated two enhancement techniques to enable the vitrification of alkali-depleted soils. The first was the placement of a starter layer of sand over the SRS soil. This technique met with limited success; the process continued to melt preferentially outward without achieving a significant downward penetration into the SRS soil. The second technique required pre-mixing of alkali materials into the soil, and was highly successful. However, pre-mixing the soils with alkali constituents detracts from many advantages of the process of vitrifying the contaminants in place without pretreatment. Consequently, Campbell and Buelt (1990) recommended developing and testing alternative ways of vitrifying SRS soil in place without prior removal for alkali mixing.

In summary, some soils may not lend themselves to ISV, but techniques exist that may address this problem. The primary alternative is to inject soluble alkaline fluxes into the soil before vitrifying it. However, the injection of a flux for the enhanced vitrification of soils has not been field demonstrated (Campbell and Buelt, 1990). Furthermore, research on ORNL soils indicated that sodium fluxes may transport contaminants (such as cesium) as gases evolve (Spalding and Jacobs, 1989).

Feed Compatibility. Feed compatibility refers to the physical compatibility of the feed with the vitrification process: can the process handle all the sizes and types of material in the feed? For example, at the Weldon Springs site, Missouri, crushed drums, structural building iron, process equipment, and a fork-lift truck are among the debris buried in the quarry (Koegler, Oma, and Perez, 1988). At INEL, buried wastes range from steel drums, to plywood boxes, to cardboard and fiberboard containers, to vehicles and large pieces of equipment (Callow, Thompson, and Weidner, 1991). Locations similar to these sites represent challenges to most remediation processes, including vitrification.

Feed materials are fed to various vitrification processes in a variety of ways, including slurries, calcined powders, shredded and chopped, bagged, boxed, drummed (as described in Chapter Four), as well as others. Ability to handle heterogeneity in the field material also varies with vitrification process. Pre-treatment by particle classification and/or other methods of feed preparation may be required at many sites prior to vitrification.

Table 7-1. Comparison of Soil Composition (wt%) from Selected Sites

	SITE				
Oxide	**Range in USA[1]**	**Hanford, Washington[1]**	**INEL Idaho[1]**	**AEDC, Tennessee[2]**	**SRS, South Carolina[3]**
SiO_2	60-93	60.9	69.6	76.0	92.5
Al_2O_3	5-17	13.6	11.4	9.0	4.8
Fe_2O_3	1-11	9.6	4.1	5.6	0.8
CaO	<1-10	6.0	10.0	6.7	0.4
MgO	<1-3	2.9	--	0.6	--
Na_2O & K_2O	<1-9	4.8	3.9	1.0	0.2
Other oxides	<1-2	2.0	1.0	1.2	1.6

[1] Buelt et al., 1987
[2] adapted from Timmerman, 1989
[3] Campbell and Buelt, 1990

Combustible Material. Combustible materials generate gases and may include combustible solids, liquids, and packages, void spaces, and organics. For example, buried, combustible wastes at INEL include wood and cardboard packaging, wood pallets, and cans and drums containing combustible organic liquids (Callow, Thompson, and Weidner, 1991). Gas-generating situations may result from the intrusion of the molten glass into void spaces and the release of entrapped air. Finally, natural organics, such as the humus in soil, may also be a source of combustible material. However, gas generation from the decomposition of humus and other natural chemicals within the soil is generally considered insignificant (Buelt, Timmerman, and Westsik, 1989). The main concern with combustible materials is that the gases they generate will carry contaminants to the glass surface and away from the melt. With ex situ processes, if combustibles present a problem, pre-treatment processes may remove much of this material and thus minimize this problem. Processes and batch compositions may also be adjusted to minimize these effects.

For ISV, combustibles are not removable if the process is to proceed in situ. Therefore, production of gases must be controlled by controlling processing conditions. Furthermore, the production rate of off-gases during the burning of combustibles must not be high enough to overwhelm the off-gas system's capacity to maintain a negative pressure during processing. If this were to occur, the fugitive emissions could possibly spread contamination. Maximum processing events that the off-gas system is capable of handling are as follows: combustible liquids (4800 kg/m of depth or 7 wt%); void volumes (4.3 m^3/combustion event); combustible packages (0.9 m^3/combustion event); and combustible solids (3200 kg/m of depth) (Buelt, Timmerman, and Westsik, 1989).

Two intermediate field tests on buried waste at INEL indicated some of ISV's abilities to handle buried combustibles. Numerous pressure spikes occurred in the first test. These pressure spikes lasted from ten to thirty seconds and were not instantaneous or characteristic of an explosion. Furthermore, pressure spikes decreased with increased depth, indicating the potential for additional soil to be placed over the buried waste to buffer the effects of the transient temperature spikes (Callow, Thompson, and Weidner, 1991).

Presence of Limiting Constituents. Limiting materials affect processing or product quality and may be present in the incoming feed. These include halogenated compounds, reducing agents, and metals of difficult types or high concentrations.

Halogenated compounds affect product durability because incorporation into the glass in high enough concentrations may produce an undesirable, porous product (USEPA, 1990a). Reducing agents such as carbon and ferrous salts may reduce arsenates and selenates to lower valence compounds that are more volatile and thus reduce incorporation efficiencies of these metals (USEPA, 1990a). Certain metals such as mercury and cadmium may be undesirable because of their difficulty to incorporate into the melt, their reduction of product quality, and/or because their volatility requires treatment in the off-gas system. Metals in high enough concentrations may also be insoluble in the glass, as all metals have solubility limitations in glasses (USEPA 1987; USEPA, 1990a). Finally, with the microwave vitrification of incinerator ashes, unburned carbon was found to affect processing. In excess of 5 wt% unburned carbon, the carbon would rapidly heat and cause arcing, thereby affecting process performance (Komatsu et al., 1990).

Methods to overcome the presence of limiting materials includes pre-treatment to reduce concentration levels and, alternatively, to increase the glass-forming additives and thereby dilute the difficult materials (USEPA, 1990a). Treatment of materials with limiting constituents may therefore be economically limited and not technically limited.

Potential Volatilization of Contaminants. Volatilization of contaminants refers primarily to inorganics, although organics may potentially volatilize before pyrolysis. By-products of incomplete organic pyrolysis may also volatilize. The potential migration of contaminants into the ambient soil during ISV could also be considered a type of contaminant volatilization. However, this issue has already been addressed in Chapter Four and will not be discussed again here.

Volatilization of contaminants increases the quantity of secondary contamination and thereby complicates treatment. At high enough concentrations, contaminants may thereby make vitrification cost prohibitive. Volatilized contaminants may be recycled to the feed to increase retention efficiencies, but this complicates treatment processes and may drive up costs. Finally, volatilized metals may potentially be recovered from the off-gas system and re-used.

Volatilized metals of concern include mercury, lead, and cadmium. Cesium volatilization during ISV treatment has been a concern at ORNL, but this problem appears to have been solved in recent tests (Spalding et al., 1991). Radium may also be a concern, although tests on Fernald K-65 residue indicate potential successful treatment (Janke, Chapman, and Vogel, 1991).

Potential Shorting Caused by Metals. The presence of metals in the feed may present another problem: shorting of the electrodes used in joule heating. Metal induced shorting is primarily a problem when the feed material has a high iron content or similar metal. These metals may sink to the bottom of the melt, concentrate there, and possibly create a conduction path that may lead to electrical shorting between the electrodes. This problem may be solved rather easily by electric melters by adding a bottom tap to remove the accumulated metals and accompanying slag. Modification of melter geometry may improve the efficiency of metal draining (Bickford, Propst, and Plodinec, 1988). Published metal limits for ISV have been 90% of the linear distance between the electrodes or 5 wt% of the melt (Buelt, Timmerman, and Westsik, 1989). However, the recent development of the EFS has made these limitations superfluous (Figure 7-1).

The EFS was developed to treat soils characterized by a high content of metals. With electrode feeding, the four electrodes that are used to initiate the ISV process are independently fed to the molten soil as the melt proceeds downward instead of being placed in the soil prior to test startup. Upon encountering a full or partial shorting condition, the affected electrodes are simply raised and held above the molten metal pool at the bottom of the melt. During this time, the melt (and molten metal pool) continues to grow downward. The affected electrodes can then be reinserted into the melt to their original depth, and all four electrodes can resume electrode feeding operations. Electrode feeding is expected to eliminate many other potential problems that can develop when processing soils containing high concentrations of metals (i.e., power limitations, void formation, electrode preplacement) (Farnsworth, Oma, and Bigelow, 1990).

The EFS has been extensively tested, including field tests at both INEL and ORNL.

At the first INEL test, some problems with electrical instabilities occurred. Electrical instabilities appeared for a variety of reasons, but under test conditions, the EFS was not able to respond aggressively to the instabilities. This was because the silicon-based coating applied to reduce electrode corrosion through oxidation would tend to stick to the glass. At times the electrodes became frozen to the cold cap and thus unable to be moved (inserted or retracted) to respond to electrical imbalances (Callow, Thompson, and Weidner, 1991).

The second INEL test was conducted without the silicon-based coating and the EFS performed well: no sticking was observed and oxidation losses were acceptable (Callow, Thompson, and Weidner, 1991).

The primary conclusion concerning the EFS from INEL tests was that uncoated graphite electrodes appear preferable to silicon-based coated graphite electrodes. Otherwise, the EFS seemed to perform well (Callow, Thompson, and Weidner, 1991).

High Cost of Energy. Generally, vitrification does require large amounts of energy to process wastes. Increased energy costs drives up process costs. Therefore, any way in which vitrification can be used efficiently will help control energy consumption, drive down costs and help

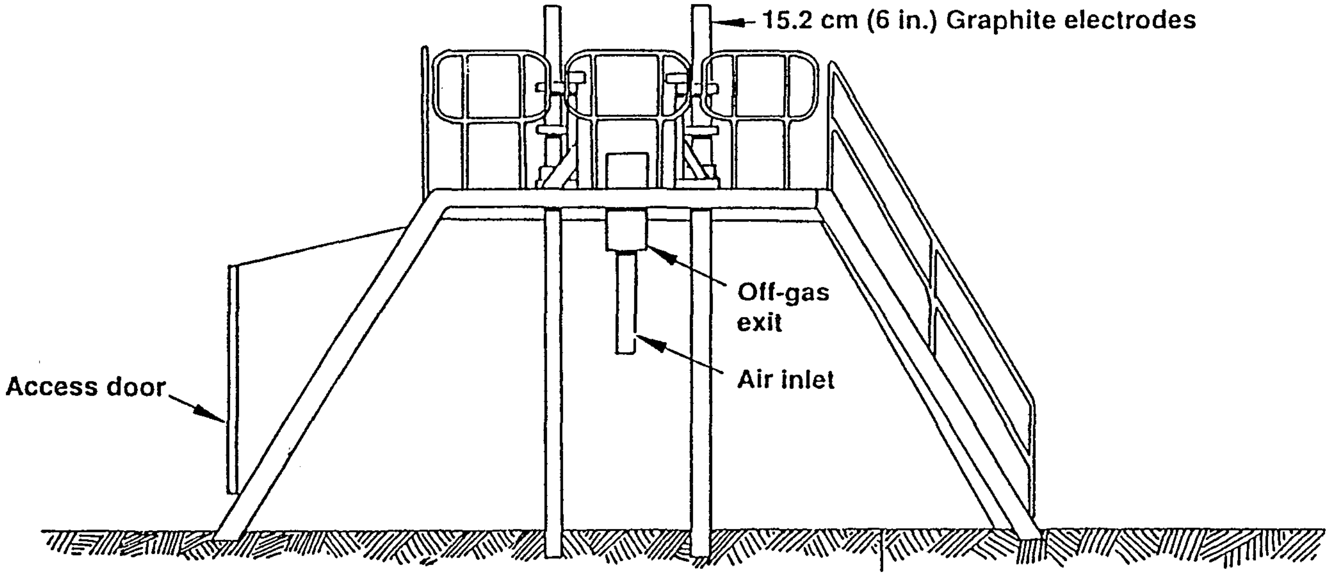

Figure 7-1. Schematic of a Pilot-Scale ISV Hood Assembly (adapted from Callow, Thompson, and Weidner, 1991)

make vitrification competitive with other treatment processes.

A primary way in which vitrification can be used efficiently is to use it at highly contaminated sites where the contamination is not diluted. For example, IRI felt that its process would not be cost effective for waste streams from small generators unless it served as a regional site for a number of generators (*The Hazardous Waste Consultant*, 1990a). Evaluation of ISV for use at ORNL indicated that it would not be applicable where groundwater had dispersed contaminants (Spalding, Jacobs, and Davis, 1989). At Faslane, in England, vitrification was used at sites highly contaminated with asbestos, but not at sites with relatively low asbestos contamination (Denner, Langridge, and Affleck, 1988). Thus, vitrification could be considered a process for treating the "hot spots."

Vitrification has also been considered for treatment of incinerator ash. This also could be considered treatment of hot spots. This is because, in one sense, the incineration of a waste stream, MSW for example, destroys many of the organic contaminants and produces a concentrated waste stream containing inorganic contaminants. Reported costs for vitrification of incinerator ash make it a cost competitive option for immobilization of inorganics in ash.

Finally, vitrification feasibility studies should consider availability of electricity and unit costs in treatment evaluations for a specific site. Energy costs may also be reduced by vitrifying during non-peak hours or seasons.

High cost of Trained Operators. Because of the complexity of vitrification, trained operators are required for both ex situ processes and ISV. This, of course, does not limit vitrification technically, but may drive up costs (USEPA, 1990b).

Depth Limitations. Depth limitations apply only to ISV and are a primary limitation of ISV at present. Currently, the greatest depth achieved has been 5 m by PNL (5.8 m by Geosafe). Sixty percent of DOD contaminated soil sites extend deeper than 5 m. If ISV could be extended to 9 m, then 90% of DOD sites would fall within ISV depths.

The primary problem appears to be heterogeneous power distributions within the melt: half of the delivered power is held in the upper third of the melt, and power decreases as depth increases. This results in a slowing of the melt advance as the melt reaches an equilibrium and finally melt advance stops. The result is a melt that spreads out more and remains shallower than predicted by early ISV modeling (see Figure 7-2). The primary need, therefore, in increasing melt depth is to increase heat near the melt floor. If this can be addressed, the present depth limit may well be doubled. Of course, deeper melt penetration will make ISV applicable to an even greater range of sites.

Possible solutions to increasing heat near the melt floor include:

- Hot-tipped electrodes
- Use of passive electrodes (EFS)
- Start melt at depth and moves upwards
- Vertical thermal barriers (walls or floors)

Hot-tipped electrodes could concentrate current at the bottom of the melt in a number of ways. These methods include:

- Attaching a molybdenum tip at the bottom of the electrode. The greater conductivity of Mo directs current through this tip.
- Covering the upper portion of electrodes with an electrically insulating material which would then funnel electricity through the tips of the electrodes.

Introduction of passive electrodes involves the intentional placement of iron-based metals in the startup layer. The metal will melt and remain at the bottom of the molten vitrified zone. This has the effect of diverting the electrical current near the bottom of the molten mass, as shown in Figure 7-3. The molten metal thus acts as a "passive" electrode that diverts electrical current and power near the bottom of the melt by providing a path of lower resistance to the electrodes. This creates higher melting temperatures, which may enhance the downward melting rate. In addition, the molten metal layer is in direct contact with the soil being vitrified. The greater thermal conductivity of the molten metal may enhance heat transfer to the soil, thereby assisting in the downward melting process. The use of passive electrodes has been shown to enhance downward melting rates (Buelt and Farnsworth, 1990).

The development of the electrode feed technique made the introduction of passive electrodes possible (Buelt and Farnsworth, 1990). As metals are encountered, the self-feeding electrodes can be withdrawn slightly from the bottom of the melt to avoid a direct electrical short. The influence of the passive electrodes can be controlled by the separation between the bottom of the graphite electrodes and the molten metal pool; decreased separation will increase the concentration of current near the bottom and increase the downward melting rate (Campbell and Buelt, 1990).

Starting the melt below ground and melting upward may be another way to increase melt depth. However, this may result in a cavity below ground level which may eventually cave in and splash molten glass into the hood area.

Thermal barriers could be placed alongside the site to be melted and prevent the movement of glass and heat into adjacent areas. Thus, the glass and heat energy would be forced downward and melt depths increased. A pilot-scale melt at PNL tested the applicability of thermal barriers. The thermal barriers were placed 6 inches from the electrodes and proved capable of withstanding melt conditions for 72 hours without evidence of degradation. Because these barriers were designed to reshape the melt and not to prohibit heat transfer, about 1 inch of sand was fused to the side of the barrier opposite the melt.

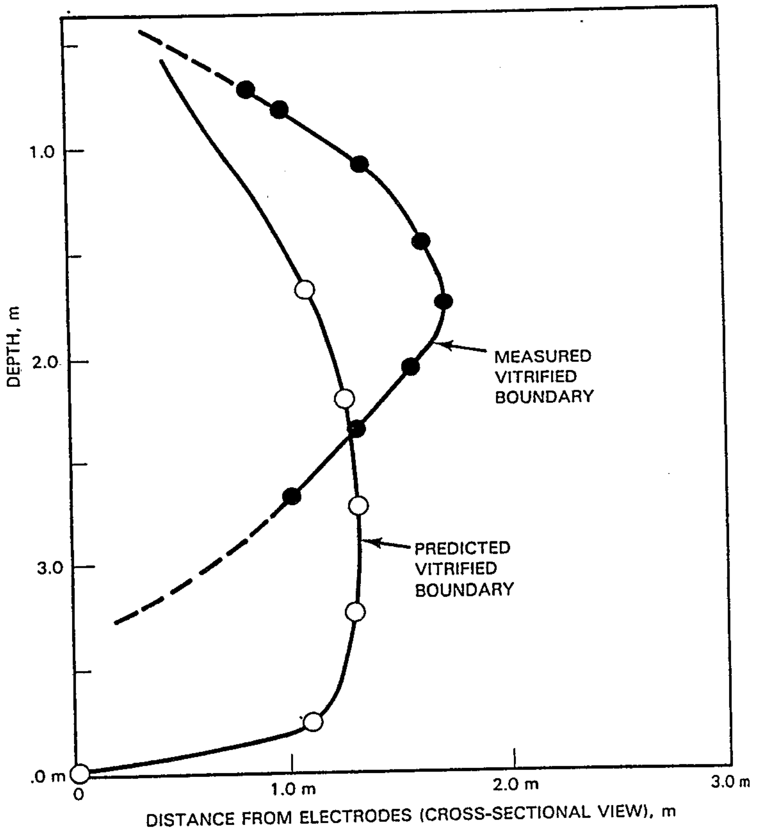

Figure 7-2. Predicted Versus Achieved Large-Scale Melt Shape (Buelt et al., 1987)

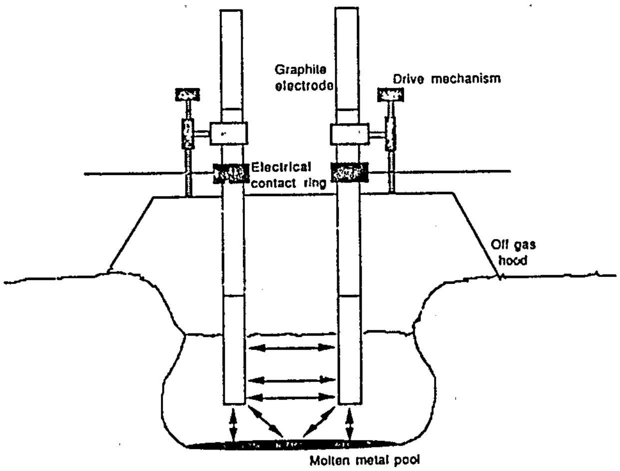

Figure 7-3. The Effect of a Molten Metal "Passive" Electrode on Electrical Current Distribution in the Melt (Campbell and Buelt, 1990)

CHAPTER EIGHT

PHYSICAL AND CHEMICAL TESTING

Performance tests include both physical and chemical tests and may be performed before treating the material to be vitrified and after treating the vitrified waste glass. For additional discussion of performance tests, please see *Stabilization/Solidification of CERCLA and RCRA Wastes* (USEPA, 1989a).

8.1 Physical Tests

Physical testing is conducted to characterize and contrast waste before and after vitrification. It provides basic information on the physical characteristics of the waste material and allows some estimate to be made on the cost of waste treatment and handling. Physical property characterization of untreated waste focuses on excavation, transport, storage, mixing, hydraulic conductivity, strength, and physical durability considerations. Physical testing of the vitrified product is one part of demonstrating the relative success or failure of the process. The physical testing methods described in this chapter may apply to both untreated hazardous wastes and treated hazardous wastes; however, the tests were not developed for use on these wastes.

This section describes some of the more common physical tests used to evaluate waste vitrification processes. These physical tests include:

- Index Property Tests: provide data that are used to relate general physical characteristics of a material (e.g., moisture content) to process operational parameters (e.g., costs).
- Density Tests: are used to determine weight-to-volume relationships of materials.
- Hydraulic Conductivity Tests: measure the relative ease with which fluids (water) will pass through a material that is to be vitrified.
- Strength Tests: provide a means for judging the effectiveness of a vitrification process by stressing the product mechanically.
- Durability Tests: determine how well a waste glass withstands environmental exposure.

Individual values of waste properties derived from specific tests are used along with other available data to make informed engineering decisions.

It is important to note that many of these tests were originally developed for testing soils and cement-like materials for physical stability for construction projects. Extreme caution must be exercised when applying these tests to untreated and vitrified hazardous wastes, and in the subsequent data interpretation. Many of the tests involve frequent handling of the waste materials; therefore, due consideration must be given to personnel protection, sample handling and disposal requirements, and other factors associated with the presence of hazardous constituents in the samples.

8.1.1 Index Property Tests

Index property tests provide data that are used to relate general physical characteristics of a material to process operational parameters. These tests are most frequently performed on untreated waste to determine the feasibility of vitrification.

One important index property for ISV is the moisture content of the material to be vitrified. The Moisture Content Test (ASTM D2216-80) determines the amount of free water (or fluid) in a given amount of material. In this test method, the term "water" refers to "free" or "pore" water, not waters of hydration. Also water in discontinuous pores is not measured by this test. The results of this test are usually expressed as fluid representing a percentage of total mass. This test is often used to determine if pre-treatment is necessary in the design of the vitrification process. An example of waste pre-treatment would be sludge drying, dewatering, or consolidation prior to vitrification.

It is also important to note that water is often not the only liquid-phase constituent in contaminated materials. The fluids may also include a broad range of liquid wastes present in solution or as nonaqueous phase liquids. This can have several effects on the performance and results of moisture content determinations. For example, if volatile organic compounds (VOCs) are present, samples should be aerated to allow volatilization of flammable VOCs before samples are oven-dried. (Of course, VOC content itself may be an important parameter to measure at some sites.) The type and level of contamination may also influence the relationship between "free" and adsorbed water.

In addition to the physical properties measured by the index property tests described above, chemical composition, thermal conductivity, fusion temperature, specific heat, electrical conductivity, and viscosity are all physical properties of the material to be vitrified that may influence process applicability and economics (Buelt et al., 1987).

8.1.2 Density Tests

Bulk density is the ratio of the total weight (solids and water) to the total volume. Bulk density, along with specific gravity and moisture content measurements, can be used to calculate a material's porosity. More commonly, bulk density values are used to convert weight to volume for materials-handling calculations and are essential for characterizing the rates at which a soil can be excavated. In addition, bulk density data provide a comparison between untreated waste and the vitrified product.

Methods of bulk density measurement include the Drive-Cylinder Method (ASTM D2037-83), the Sand-Cone Method (ASTM D1556-82), and the Nuclear Method (ASTM D2922-81). The data from each are sufficiently accurate for calculating densities. Selection of a method is usually based on ease of use. Laboratory determination of specific gravity can supplement these measurements.

8.1.3 Hydraulic Conductivity Tests

Hydraulic conductivity, often referred to as permeability, is a measure of the resistance of a material to the passage of fluids. Permeability tests are performed to estimate the quantity and flow rates of water through a material under saturated conditions. Laboratory permeability testing consists of applying a hydraulic head of water to one end of a specimen and measuring the flow through the specimen.

There are two basic types of permeability tests: constant-head and falling-head. The constant-head test allows relatively large quantities or water to flow through the sample and be measured. This test is suitable for materials with a permeability greater than 10^{-6} cm/s. The falling-head test, which allows for more accurate measurement of small quantities of water, is more suitable for materials with a permeability of less than 10^{-6} cm/s (Carter, 1983).

Sand, a highly permeable material, has a permeability on the order of 10^{-2} cm/s. Clay, a material that is used to line lagoons and surface impoundments, can have permeability on the order of 10^{-6} cm/s or less and is considered relatively impermeable.

As described in Chapter Seven, the permeability of a soil may be an important factor in estimating the effectiveness of ISV for a particular site. At high moisture contents, ISV will have to first boil off the water at the vitrified site before a glass melt will be formed. Thus, at high moisture content, if the permeability of the soil is too high (above 10^{-4} cm/s), water will move into the melt site faster than it can be boiled off and the melt will not form (Buelt et al., 1987).

8.1.4 Strength Tests

Strength-test values indicate how well a material will hold up under mechanical stresses created by over-burden and earth-moving equipment. It can also be used to give some idea of how well a waste glass will resist fracturing and thus increasing its surface area. This test, along with the chemical leach test (see below), helps form an estimate of the product durability.

A common strength-test is Unconfined Compressive Strength of Cylindrical Cement Specimens (ASTM D1633-84) However, several other strength tests may be performed in addition to or in place of this test, depending on the intended use of the data.

The EPA considers a solidified waste material with a strength of 50 psi to have a satisfactory Unconfined Compressive Strength (USEPA OSWER Directive, No. 9437.00-2A). This minimum guideline of 50 psi has been suggested to provide a stable foundation for materials placed upon it, including construction equipment and impermeable caps and cover material.

The minimum required Unconfined Compressive Strength for a treated material should be evaluated on the basis of the design loads to which the material will be subjected. The anticipated over-burden pressure and other loads, along with appropriate safety factors, can be used to calculate this.

Typical construction and compaction equipment can generate very high contact pressures of 1000 psi or more (e.g., sheepsfoot rollers), but surface contact pressures on the order of 50 to 100 psi are more common. This surface load is attenuated with depth so that bearing pressures are reduced to values on the order of 10 to 20 psi at a depth of 2 feet and 3 to 7 psi at a depth of 5 feet below grade. Overburden pressures will usually be on the order of 0.75 to 1.0 psi per foot of depth. If guidelines such as these are used, the stresses to which the waste glass will be subjected can be predicted, and design criteria can be selected accordingly.

8.1.5 Durability Tests

Durability Testing evaluates the resistance of a waste glass to degradation due to external environmental stresses. The tests are designed to mimic natural conditions by stressing the sample through: (1) freezing and thawing; and (2) wetting and drying. The waste glass specimens may undergo repeated cycling during the testing. Unconfined Compressive Strength, flexural strength, permeability, or other performance-based tests may be conducted on the glass samples after each cycle to determine how the physical properties of the waste change as a result of simulated climatic stresses. The number of cycles a material can withstand without failing can be used to judge the mechanical integrity of the material.

These tests relate to the long-term stability of the sample. If the results show low loss of materials and retention of physical integrity after testing, then the chemical composition of the vitrified product is adequate. If the test results show a large loss of material and loss of physical integrity, then various chemicals may have to be added to the feed material to provide the long-term stability needed.

Poor durability results often can be addressed by a change in design and should not be used as automatic grounds for exclusion. For example, materials that fail freeze-thaw durability testing can be placed below the frost line to mitigate their poor durability property.

8.2 Chemical Tests

This section discusses leaching tests, the tests most often used to evaluate the performance of vitrification as a treatment process for hazardous waste.

In the field, leaching of hazardous constituents from waste glass is a function of both the intrinsic properties of the waste form and the hydrologic and geochemical properties of the site. Although laboratory physical and chemical tests can be used to define the waste form's intrinsic properties, the controlled conditions of the laboratory environment are usually not equivalent to changing field conditions. At best, laboratory leaching data can simulate the behavior of waste forms under "ideal", static (conditions at one point in time), or "worst-case" field conditions. Presently, leach tests can be used to compare the effectiveness of various waste glasses, but they have not been verified for determining the long-term leachability of the waste.

8.2.1 Toxicity Characteristic Leaching Procedure (TCLP) (Federal Register, 1986)

This test involves the definition of a toxicity characteristic waste under the RCRA hazardous waste regulations. The test is defined in 40 CFR 261 as follows. Waste samples are prepared by crushing the wastes to pass through a 9.5-mm screen, and liquids are separated from the solid phase by filtration through a 0.6 to 0.8 µm borosilicate glass-fiber filter under 50 psi pressure. Two choices of buffered acidic leaching solutions are offered under TCLP, depending on the alkalinity and the buffering capacity of the wastes. Both are acetate buffer solutions. Solution No. 1 has a pH of about 5; Solution No. 2 has a pH of about 3. The leaching solution is added to a Zero Headspace Extractor (ZHE) at a liquid:solid ratio of 20:1, and the sample is agitated with a National Bureau of Standards (NBS) rotary tumbler at 30 rpm for 18 hours. The leaching solution is filtered, combined with the separated liquid waste fraction, and analyzed for specific organics and metals.

8.2.2 Materials Characterization Center Static Leach Test (MCC-1P) (MCC, 1984)

This static leaching test was developed for HLW. It involves leaching of a monolithic waste form with water (ASTM Type I or II) at a volume of leaching solution to surface area of solids (V/S) ratio of between 10 and 200 cm. The period and the temperature of extraction vary, depending on the schedule selected. MCC-1P test results can be combined with those from extraction tests (e.g., TCLP) to determine a range of leachate concentrations in the short term (well-managed site with waste form intact) and the long run (waste matrix has been subjected to many years of environmental stress and is fractured).

8.2.3 Materials Characterization Center MCC-3 Test

The MCC-3 agitated powder leach test is very similar to the MCC-1 test procedure with two exceptions: the glass is in a powdered form and the glass powder and leachant are agitated by rotating the container. This produces an elemental leachate concentration that may be more representative of dissolution under saturated conditions. Leachate saturation is achieved more rapidly in the MCC-3 test because higher surface area to volume ratios are used than in the MCC-1 test. The powder MCC-3 test is also very useful in cases where multiple phases are present in the waste form. Because the MCC-1 test uses a cut monolith for testing, results are often affected by the representation of the different phases on the surface of the monolith. The MCC-3 uses powdered samples thereby allowing all phases to contact the leachate (Koegler et al., 1989).

8.2.4 Product Consistency Test (PCT)

The PCT evolved from the MCC-3 test and was developed for evaluating high-level vitrified waste forms from the DWPF at SRS. The test can be performed remotely and is reproducible. Leachate is monitored for metal concentration and pH. The glass is crushed, sized, rinsed, and submerged in deionized water at 90°C for 7 days (Jantzen and Bibler, 1990). This test is being evaluated as an ASTM standard test.

8.2.5 American Nuclear Society Leach Test (ANS-16.1, 1986) (ANS, 1986)

A "quasi-dynamic" leach test, ANS-16.1, can be applied to vitrified low-level and hazardous wastes. A monolithic cylinder (length:diameter of 0.2 to 5.0) is leached with demineralized water applied at a V/S ratio of 10 cm under ambient temperatures. At the start of the experiment, the sample is rinsed to obtain zero contaminant concentration at the surface of the sample. Afterwards, the sample is immersed in water, which is replaced after 2 hours, 7 hours, 24 hours, 48 hours, 72 hours, 4 days, 5 days, 14 days, 28 days, 43 days, and 90 days.

The results of the leaching test are recorded in terms of cumulative fraction leached over the total mass in the waste form, against time. Calculations are then used to derive an effective diffusion coefficient, De (cm^2/s), and a leachability index (LX = -log De). The LX values range from 5 (De = 5-10, rapid diffusion) to 15 (De = 10-15, very slow diffusion).

8.2.6 Leaching Test Selection and Interpretation

As mentioned in the preceding discussions, leaching tests produce results that are not directly applicable to leaching behavior in the field. Nevertheless, the results of several leaching tests or of leaching tests combined with physical tests or microscopic techniques can be used as indicators of field performance and environmental impact.

When used for comparative purposes, results from several leaching tests can help identify field conditions that may result in different concentrations of waste leaching. Therefore, these data may be used to select or design waste facilities that will minimize the leaching of hazardous constituents from the wastes. The data also may be used to predict the leaching of waste glass at different stages in time. For example, a closed facility that has a cover which is maintained (i.e., a 30 year post-closure period) and minimizes precipitation infiltration, leaching conditions may be similar to those of the MCC-1P test (i.e., static hydraulic conditions).

In the few cases where the actual field leaching solution is well known, use of this solution in the laboratory tests may yield more representative results. When the site leaching solution is used, however, the results may be relevant only to field leaching conditions in the short term because the site hydrogeochemistry may change over the long run.

CHAPTER NINE

PROCESS EVALUATION

Technology screening is an important part of evaluating any technology. In this chapter, examples of vitrification comparison studies are presented, scaling-up problems are discussed, and cost categories for in situ and furnace vitrification are described.

9.1 Selection of Vitrification Processes

In this section, two studies evaluating vitrification processes are described. These studies are presented as examples of ways in which vitrification processes may be evaluated. Because of the differing goals and identified waste streams in the two studies, the questions asked and the conclusions drawn differed. In addition, the processes evaluated differed between the two studies. Evaluation of vitrification processes should proceed with site or waste specific goals in mind: the questions asked will shape the conclusions drawn.

Bickford et al. (1991) evaluated four vitrification processes: calcination followed by pot melting, a modified commercial melter, a HLW joule-heated melter, and a stirred melter. Each melter was evaluated for process characteristics in treating two groups of waste. The first step in this study was to identify a series of desired process characteristics (Table 9-1). (Please note that the evaluation for only one of the waste groups is presented in Table 9-1.) These characteristics were ranked on a scale of 0 to 10 for their relative importance in treating each of the two waste groups. Then, each melter system was rated for its ability to meet each characteristic on a scale of 1 to 10 and assigned a decimal value accordingly (i.e., a "5" became a "0.5"). The score of each melter system for each of the desired characteristics was multiplied by the relative importance value of that characteristic. These values were summed to establish the total rating.

In the second study (Haz Answers, 1991), conducted for INEL, a variety of thermal processes were evaluated for Radioactive Waste Management Center (RWMC) waste. A total of 27 technologies made up the preliminary list of thermal technologies. Only those technologies which applied to sludge, solid combustible, or solid inert wastes passed the initial screening of the preliminary list and were evaluated in detail. Each of the remaining 16 technologies were scored on the basis of 7 identified evaluation criteria. These criteria were chosen as the most important site-specific aspects to be considered in making decisions concerning the treatment of RWMC wastes. A relative index was applied to the evaluation criteria in order to weight the evaluation criteria according to perceived importance in treating RWMC wastes (from a high of 0.25 for "Final Waste Form" and "Versatility" to a low of 0.05 for "Cost"). Finally, each technology was scored on a scale of 1 to 5 for each of the evaluation criteria and then multiplied by the weighted factor of that evaluation criteria. Scores were summed. The results of this summary are presented in Table 9-2.

9.2 Initial Testing and Scaling-Up

The question of testing a process and then scaling up to a full-scale operation is a common problem in dealing with hazardous material. This section describes some of the general issues in this procedure and address some specific questions that may be important at the bench-scale. Variations in site and waste characteristics drive the development of objectives for a particular site or waste, and these objectives may influence the nature of the treatability study.

9.2.1 Treatability/Bench-Scale Testing

Treatability/bench-scale testing involves the performance of various physical and chemical tests on actual contaminated materials from the site, followed by engineering-scale melt testing on the materials. Treatability testing is used to:

- Demonstrate that the technology is applicable to the specific soil/waste combinations at the site.
- Produce contaminant-related performance data necessary to support permitting activities.
- Develop design data necessary to support cost estimates and quotes.

Table 9-1. Determination of Preferred Melter System for Beta-Gamma, Low-Level Mixed, Inorganics (Heavy Metals), Asbestos, Organics, and Soils Wastes (Bickford et al., 1991)

	Characteristics																
Melter Type	Raw Materials Cost	Waste Loading	Homogeneity	Melter Life	Melter Repair	Waste Variation	Product Sampling	Small Scale	Large Scale	Portability	Drain/Restart	Generic Licensing	Melter Costs	Melter Disposal	Various Feed Connections	Various Off-Gas Connections	**Total Rating**
Relative Importance	6	6	8	10	4	10	10	1	10	5	7	8	8	2	10	8	113
Calciner/Pot Melters	3	5	4	4	3	4	2	0	3	3	6	4	4	1	3	2	51
Modified Commercial	6	6	6	10	2	8	8	0	10	2	2	6	8	1	10	6	91
HLW Joule Heated Melter	3	5	6	10	1	6	8	0	8	3	2	6	3	1	8	4	74
Stirred Melter	5	6	8	4	4	7	9	1	6	5	7	6	6	2	6	4	86
Indicates Preferred System																	

- Produce samples of residual product for use in meeting regulatory requirements.
- Define materials of construction for processing equipment. This is particularly important for high temperature processes such as vitrification.

The cost of treatability testing is comparatively low and permits early screening of various processes before significant money and effort are spent on a technology which may not be applicable to a specific site. ISV treatability studies usually can be completed within eight to ten weeks after project initiation (Hansen and FitzPatrick, 1989).

Questions which may be addressed in vitrification treatability studies:

- Composition of the feed
- Total composition of contaminants in the field
- Time requirements for the high-temperature processing of the feed
- Melt parameters, such as temperature, oxidation-reduction conditions, etc.
- Need to add any materials, such as fluxing agent, etc.
- Total concentration of contaminants in the product
- Leaching behavior of the product.

9.2.2 Scale-Up/Field Testing

Once bench-scale tests have demonstrated that the process under consideration is applicable to site parameters, pilot-scale tests are often conducted. The primary objec-

Table 9-2. Criteria Raw Scores and Weighted Overall Scores for INEL Thermal Process Evaluation Study (Haz Answers, 1991)

Technology Name	LDA	VRSL	THRU	FWF	EFLT	COMP	COST	Overall Weighted Score
Slagging kiln	5	5	3	3	3	2	1	3.4
Fluidized bed	5	3	5	1	2	3	5	2.9
Multiple hearth	5	1	3	1	3	5	4	2.6
Rotary kiln	5	5	5	1	1	4	5	3.5
Controlled air	5	1	3	1	5	5	4	2.8
Cyclone	5	1	5	1	5	5	5	3.0
Low temperature thermal separator	2	2	5	1	5	4	5	2.8
Infared furnace	4	2	5	1	5	3	5	2.9
Molten salt furnace	3	1	3	1	5	2	4	2.1
Plasma centrifugal reactor	2	4	4	3	3	1	4	3.0
Plasma arc furnace	2	4	4	3	3	2	2	3.2
Conventional temperature pyrolysis	4	1	3	1	4	4	4	2.4
Microwave discharge	3	2	1	1	5	5	3	2.7
Molten glass furnace	4	4	5	2	5	3	4	3.6
In situ vitrification	3	4	3	5	4	5	5	4.3
Microwave melter	2	1	1	3	4	5	2	2.6

LEGEND:

LDA = Level of Development and Availability
VRSL = Versatility
THRU = Throughput
FWF = Final Waste Form
EFLT = Effluents
COMP = Complexity
COST = Cost

tive of pilot-scale tests is to confirm that bench-scale test results will be applicable on a larger scale. This is accomplished by testing a portion of the actual site or a simulation of an actual site. The testing typically evaluates process operations effectiveness, off-gas behavior of volatile or entrained materials, potential costs, and potential processing problems (Lominac, Edwards, and Timmerman, 1989).

9.2.3 Scaling-Up Case Studies

The scaling-up process of Geosafe's ISV and Retech's PCR (both described in Chapter Three) will be presented in this section to give some idea of the steps involved in this process.

9.2.3.1 Scaling up of ISV

The scaling up process of ISV used at PNL is described in this section. Development and deployment of the large-scale ISV system is the ultimate goal of the ISV program, because it is less costly to operate, and it is more adaptable to numerous types of waste sites than the pilot-scale system. The cost of vitrifying a given waste volume with the large-scale system is less than that of the pilot-scale system. The large-scale system is more adaptable because of its high-capacity off-gas system, which can process off-gas at a rate of 104 standard m^3/min, is better equipped to contain sudden gaseous releases from combustible and other gas-generating wastes. Nevertheless, the pilot-, engineering-, and bench-scale systems provide important data that are used to determine the performance of the large-scale system at a significantly reduced development cost. The scale of all four development units for DOE is described in Table 9-3. Descriptions of these development units follow in the text.

Bench-Scale System. The bench-scale system is used primarily to verify ISV processability and off-gas characteristics from alternative types of soil and waste inclusions. The bench-scale unit has been used on many occasions for new soil and waste types as a precursor to larger-scale testing or onsite demonstrations. It is relatively inexpensive to operate, and it is instrumental in determining the applicability of ISV to various waste types.

Engineering-Scale Tests. One of the primary developmental tools for ISV has been the engineering-scale laboratory test, which is operated in the PNL developmental laboratory. The engineering-scale system has many flexible design features for testing new concepts. Because of its smaller scale, the engineering-scale system can test new concepts at a reduced cost while maintaining a high level of confidence in its predictive capabilities for larger-scale operations. Many of the analyses of ISV process limits have been based on tests conducted with the engineering-scale unit (Buelt et al., 1987).

Pilot-Scale Tests. The pilot-scale system is a portable field system. The pilot-scale system is intermediate in scale between the engineering-scale tests and the larger scale tests and performs an important linking step in the scaling-up of ISV. The pilot-scale ISV system has travelled to ORNL twice, INEL twice, and AEDC once for onsite testing in contaminated areas.

Large-Scale Tests. Large-scale ISV tests are used to verify that designs indicated at smaller-scale tests do indeed work effectively with the large-scale system. Development of the large-scale ISV system has proceeded in two steps: large-scale operational acceptance tests and large-scale verification tests. The operational acceptance tests verified conformance of processing characteristics to the established functional design criteria relevant to the large-scale tests on actual waste streams. The verification tests verified the effectiveness of process modifications identified during the operational acceptance tests in readying the process for actual testing.

9.2.3.2 Scaling-up of Retech's Plasma Centrifuge Reactor (PCR)

Retech went through a similar scale-up process in the development of its PCR (Eschenbach, Hill, and Sears, 1989). Their scale-up process went through three phases.

Phase I (1985-86) consisted of a series of tests conducted with a transferred-arc plasma on materials (metals, glass, rubber, plastics, filter elements, etc.) typical of materials which may get contaminated with radioactivity. These tests demonstrated the feasibility of a transferred arc plasma as a volume reduction process. As a result of these tests, it was concluded that the addition of oxygen or air as an oxidant in the plasma gas (argon in Phase I tests) would be desirable in order to convert hydrocarbons to CO_2 and water instead of soot, CO, and hydrogen.

Phase II (1986-88) saw the development of the first PCR. This quarter-scale reactor had a 0.46m (1.5 ft.) reactor well and a 150 kw transferred-arc plasma torch operating on air or an oxygen-argon mix. Tests were conducted on dirt spiked with water and organics. These tests showed that the product passed standard leach tests for the non-volatile components retained in the glass. Difficulty with pouring the glass indicated that the melt was too viscous.

Phase III (1988-1989) focused on the operations of a larger PCR. This PCR had a 1.8 m (6 ft.) reactor well and a 600 kw plasma torch. It was tested with a soil spiked with 15% oil. Tests with this PCR showed that air proved to be the most satisfactory plasma gas: argon proved to be unstable and the O_2/argon mix corroded the electrodes. Results indicated that DRE's of 99.99% to 99.999% were obtained. These tests also confirmed that the changes in the reactor well permitted pouring of the molten glass. Waste feeder problems were also identified during these tests.

Table 9-3. Testing Units For Developing ISV Technology

Equipment Size	Electrode Separation	Glass Block Size
Bench Scale	0.11 m	1 to 10 kg
Engineering Scale	0.23 to 0.36 m	0.05 to 1.0 t
Pilot Scale	1.2 m	10 to 50 t
Large scale	3.5 to 5.5 m	400 to 800 t

By testing the PCR in increasing-scale tests, Retech was able to establish that their system could potentially treat heavy metals and organic waste with favorable results. Furthermore, problems encountered with smaller-scale systems enabled Retech to refine their process design before encountering these problems in a large-scale PCR.

The PCR is now being further tested and developed at the Component Development and Integration Facility (which is under the administration of INEL) for testing in the EPA Superfund Innovative Technology Evaluation (SITE) program (Viall, Sears, and Eschenbach, 1990). A larger PCR is located in Basel, Switzerland (Schlienger and Eschenbach, 1991).

9.3 Cost

In addition to technical feasibility and questions of scaling up, costs are also an important component in the evaluation of the applicability of any remediation process. The following section is intended to identify key cost variables of vitrification processes—such as site preparation, mobilization/demobilization, energy costs, etc.—and to summarize cost information developed to date. The reader is cautioned that the cost information is presented for summary and evaluation purposes only, and should not be used for feasibility study cost estimates nor for comparative purposes. Furthermore, comparisons among various cost studies may be misleading because of variations in:

- cost variables included in cost estimates (such as overhead or profit for commercial vendors, etc.)
- values assumed in estimating cost variables (variation in location and extent of contamination, site clean-up objectives, etc.)
- type of vitrification process evaluated (in situ vs. ex situ vs. ex situ process type)
- waste type (radioactive vs. hazardous waste)

Cost estimates also can vary with time, and cost estimates made for one technology in one year may not be comparable with cost estimates made for another technology in another year. Furthermore, costs estimates for the same technology may have been developed in different ways by different researchers. For example, in estimating costs for the furnace melter vitrification of contaminated soils, researchers may or may not have included the cost of excavation of the soils in their estimate. Finally, as vitrification is in its early development stages as a waste treatment, costs are not established on actual projects and are often estimates.

In an attempt to clarify the major sources of costs, this section will discuss ISV and furnace melters separately. Under each discussion, categories of cost and estimated costs will be described. In addition, the furnace melter discussion will include a description of several methods considered at a DOE site to reduce overall treatment costs. The intent of this section is that the reader gain an understanding of cost categories which are significant areas of concern in managing costs, and a general idea of actual vitrification costs.

9.3.1 ISV Costs

This section describes cost categories for generic ISV application.

9.3.1.1 Cost Categories for ISV

The main costs for ISV vary depending upon electrical costs for a particular geographic region and soil moisture content. The moisture within the soil must be driven from the melt zone before vitrification can begin. ISV costs can be categorized into five subsections (Liikala, 1991):

1. Site Activities
2. Equipment
3. Operations
4. Expendables
5. Electrical Power

Cost items that fall within these categories are identified in Table 9-4. Categories are briefly summarized below.

In addition to the costs identified above, another area of cost is treatability testing. Treatability testing includes the performance of various physical and chemical tests on actual contaminated materials from the site and engineering-scale ISV melt testing on the materials. The cost of treatability testing is in the range of $40,000 to $70,000 or more, depending on application. Unusual analytical requirements, such as those posed by dioxin analyses, may increase the costs (Timmons, FitzPatrick, and Liikala, 1990).

The cost of equipment mobilization and demobilization depends on transport distance to and from the site. The combined total of these costs may be estimated at $50,000 plus $50 per transport mile. Typical total mobilization/demobilization costs fall in the range of greater than $100,000 to as much as $200,000 (Timmons, FitzPatrick, and Liikala, 1990).

Finally, the reader should be aware there is profit involved when buying commercial services.

Table 9-4. Major Components of ISV Costs (adapted from Buelt et al., 1987)

SITE ACTIVITIES

- Transporting equipment to and from site
- Clearing vegetation
- Rough grading
- Removing overburden
- Acquiring and applying backfill material

EQUIPMENT

- **Power**
  - Portable generator
  - Power lines
  - Substation
  - Power cables
- **Mechanical**
  - Electrode frame and hood
  - Drilling machinery
  - Crane
  - Front-end loader
- **Off-gas and monitoring**
  - Off-gas treatment system
  - Radiation and off-gas monitors/alarms

OPERATIONS

- **Process preparations**
  - Drill holes and place electrodes
  - Spread graphite starter material
  - Position frame and hood, secure electrodes
  - Connect power cables and off-gas line
  - Vitrify
  - Disconnect power cables and off-gas line
  - Hood fixation
  - Remove frame and hood
  - Backfill vitrified area
  - Move power cables for next setting
- **Process operations**
  - Off-gas treatment system
  - Power system
  - Radiation or toxic chemical monitoring
  - Melt verification
  - Off-gas secondary waste disposal

EXPENDABLES

- Electrodes
- Secondary Wastes

ELECTRICAL POWER

Site Activities. Activities included in site preparation include soil staging (if necessary), electrode placement, set-up of ISV process trailers, electrical connections, and subsidence backfilling. Site activities include transporting equipment to and from the site, clearing vegetation, grading the ground, removing overburden, and acquiring and applying backfill material as needed. If uncontaminated overburden could be removed safely, it would always be advantageous to do so from a cost standpoint. For example, removal of the top meter of clean soil from a 2700-m^2 site would cost less than \$10,000, compared to the hundreds of thousands of dollars needed for labor and power charges to vitrify the same area to a 1-m depth. In short, site activity costs will be insignificant when compared to equipment, labor, and electrical power, for the majority of potential ISV applications (Buelt et al., 1987).

Equipment. The ISV process trailers are the major equipment required on-site. The only additional equipment required are diesel generators—if high-voltage line power is not available, a crane, and a front end loader or dozer.

Electrical equipment requirements are determined by the voltage and current demands of ISV: the high voltage at the beginning of processing requires sufficient insulation while the high current at the end of processing requires sufficient conduction capacity. For example, the high level of current (4000 A) requires that six 750-mcm power cables be used for each of the four electrodes (Buelt et al., 1987).

Two pieces of heavy equipment are necessary for ISV operations: a crane for transporting the electrode frame and hood from one setting to the next and a front-end loader for backfilling and site preparation. Purchase of this equipment may be more cost effective than rental because of the higher cost of renting these types of equipment (typically several hundred dollars per day) for the duration of projects that last from 9 months to 10 years (Buelt et al., 1987). If the EFS is not used at a particular site, then a drilling or auguring machine for placing the electrodes in the ground may also have to be purchased.

Operations. The time required for each setting of the electrode frame and hood is the sum of the time required to vitrify the soil to the predetermined depth plus the time required to move the off-gas equipment to the next setting. The ISV processing rates are generally 4 to 5 tons/hour. Typically, less than 24 hours are required to restage the hood and the ISV trailers between subsequent melts. Calculated time per setting for the large-scale systems as a function of moisture content is shown in Table 9-5. The effects of moisture content on vitrification rate and operating time are evident from these vitrification times (Buelt et al., 1987).

Total project time is equal to the time per setting multiplied by the number of settings. The number of settings depends on the dimensions of the site to be vitrified and the area vitrified per setting. This latter characteristic is a function of electrode spacing and acceptable allowances for overlap between vitrified blocks. For example, given the parameters estimated in Table 9-6, a contaminated area 90m x 30m is estimated to require 48 separate ISV settings.

Table 9-5. Time Requirements for Each ISV Setting (Buelt et al., 1987)

	Large Scale, 5-m Depth, 5% Moisture, h/setting	Large Scale, 5-m Depth, 25% Moisture, h/setting
Vitrification	90	117
Moving Equipment	16	16
Total	106	133

Table 9-6. ISV Electrode Spacing and Vitrification Settings (Buelt et al., 1987)

Parameter	Large Scale, 5-m Depth
Electrode spacing	4.5m
Separation between electrodes of adjacent set	3.0m
Width vitrified per set	7.8m
Area to be vitrified	90m x 30m
Set matrix (rows x colulmns)	4 x 12
Number of settings	48

Personnel and their estimated hours for large-scale process preparation are identified in Table 9-7. These personnel are required at scheduled intervals: once per setting of the off-gas containment hood.

Personnel and their estimated hours for large-scale process operations are identified in Table 9-8. A typical ISV melt requires two operators per shift: a shift engineer and an ISV technician dedicated to operating the system while power is supplied to the electrodes. An engineer is included on day shift as an operator (see Table 9-8) and to provide technical resolution of any operational problems. Maintenance and radiation monitoring personnel (required during the vitrification of radioactive wastes) are included in the operations on an estimated part-time basis.

Expendables. Electrodes have been considered one of the major expenses of ISV because the cost of the molybdenum used in the electrodes is around $20 per

Table 9-7. Manpower Requirements for ISV Process Preparation (Buelt et al., 1987)

Job Classification	Manpower Rate, Average Man-Hours/Setting
Electrician	4
Laborer	34
Operator	19

Table 9-8. Labor Estimate for ISV Processing Operations at a Radioactive Site (Buelt et al., 1987)

	Workers Per Shift			Total
Job Classification	Day	Swing	Graveyard	Man-Hours/Day
Engineer	1	0	0	8
Maintenance	0.5	0	0	4
Operator (Technician)	1	2	2	40
Radiation monitor[(a)]	0.25	0.25	0.25	6
Total				58

(a) Radiation monitoring personnel would not be required for a hazardous waste site.

pound. After a single melt, the electrodes are not reusable due to the large crystalline growth of the molybdenum (Liikala, 1991). However, the development of the EFS permits the use of all-graphite electrodes instead of the molybdenum/graphite electrodes previously used. Thus, electrode costs will be substantially reduced if the EFS is used.

In addition to electrode costs, a cost must be included for disposing of the secondary liquid wastes that are collected in the off-gas system. Approximately 200 L (530 gal) per large-scale setting must be disposed of at a cost of \$0.26/L (\$1.00/gal). For the site configuration given in Table 9-9 this results in additional charges of \$25,000 (\$1.85/m^3) (Buelt et al., 1987).

Electrical Power. Electrical power requirements are a significant portion of the operating costs. Energy costs for high voltage line power varies greatly with location, ranging from as low as 2.5 cents per kwhr on the west coast to 8 cents per kwhr in the Midwest and east coast. A diesel generator may conceivably be used in locations inaccessible to power lines or where electrical power is prohibitive. Cost for use of diesel generators is equivalent to about 8.25 to 13 cents per kwhr.

The power requirements and estimated costs for the ISV vitrification of low (5%) and high (25%) moisture content materials are given in Table 9-9 for a specific hypothetical application. Also shown is the annual vitrification rate which is based on an 80% operating capacity of the ISV model prediction (Buelt et al., 1987).

9.3.1.2 Estimated Cost for ISV

As indicated in Table 9-10, the on-site service cost of ISV processing may range from \$96 to \$390 per ton of material processed for the references cited. These estimates should not be considered as firm estimates appropriate for all sites and all applications. Rather, they serve as rough ISV cost estimates. Site characteristics and clean-up goals will play important roles in modifying these estimates. Furthermore, the parameters considered have not always been identified, or they may differ from study to study. For example, Buelt et al. (1987) included elements of direct and indirect cost, such as labor, materials, energy, equipment amortization, and contractor overhead and profit, but ignored treatability costs. Carpenter and Wilson (1988) calculated their estimates from the following formula:

Cost, \$/ton = (\$13 dredging) + (\$8-80 transportation)
+ (\$96-210 treatment) + (\$46 redeposition)
= \$163-349

Thus, great care should be used when examining these cost estimates.

Table 9-9. Power Requirements for ISV Rate as a Function of Moisture Content (Buelt et al., 1987)

Moisture Content	Energy Requirement kWh/setting	Annual Vitrification Rate, m^3/yr	Cost/Setting (@ \$0.05/kWh)
5%	302,000	15,300	\$15,100
25%	392,000	12,200	\$19,600

Table 9-10. Sample ISV Cost Estimates (\$/ton)

Year	Cost range (\$/ton)	Reference
1985	\$117-165[a]	(Buelt et al., 1987)
1986	\$ 96-210[a]	(USEPA,1986)
1988	\$163-349[a]	(Carpenter and Wilson, 1988)
1989	\$166-175[a]	(Koegler et al., 1989)
1990	\$103-382[a]	(USEPA, 1990c)
1991	\$360-390	(Landau Associates, 1991)

[a] Calculated from reported figures assuming 1.2 tons/yd^3.

Table 9-11. ISV Equipment Costs (Koegler et al., 1989)

Equipment	Estimated Costs ($1000)	Percentage of Total Cost
Engineering and Design	500	3
Equipment Mobilization (6 systems)	540	3
Transformers (6 required)	1,500	9
Off-Gas Hood and Line (6 required)	3,600	21
Off-Gas System (3 required)	9,000	51
Backup Blower System (3 required)	600	3
Power Lines (6 systems)	120	<1
Electrode Power Cables (6 systems)	240	1
Portable Generators (3 systems)	300	2
Equipment Demobilization (6 systems)	780	4
Electrode Placement Machinery (1 system)	120	<1
Crane (1)	130	<1
Front End Loader (1)	80	<1
Total Equipment Costs	**17,500**	

Weldon Spring Site. If cost estimates are examined on a percentage basis, those factors contributing most greatly to costs can be identified. Costs were carefully broken down in evaluating the treatability of ISV to the Weldon Spring site in Missouri (Koegler, Oma, and Perez, 1988; Koegler et al., 1989). Examination of this data permits a more detailed discussion of the relative importance of ISV cost categories.

The Weldon Spring site comprises a 9-acre former limestone quarry, a 52-acre disposal area for raffinate waste (the less soluble residue remaining after chemical extraction), and a 169-acre mothballed uranium-feed materials plant. The quarry, about 4 miles south of the main site, contains an estimated 95,000 cubic yards of rubble and soil contaminated with trinitrotoluene (TNT), dinitrotoluene (DNT), uranium, thorium, and their decay products. The waste material is piled 40 feet above the floor of the quarry, and most of the waste is covered by several feet of soil. Vegetation covers the quarry surface and the lowest area is covered by water. Where a cross section is visible, a large amount of metal (e.g., crushed drums, sheet metal, structural building iron, and process equipment) protrudes from the soil. Large pieces of equipment such as tanks, a fork-lift truck, and up to 3000 drums are also buried, although ground-penetrating radar or similar techniques have not been used to locate these large items. The water table is about 15 feet above the floor of the quarry, and the standing water level is about 6 feet above the water table (Koegler, Omar, and Perez, 1988).

Table 9-11 gives an itemized capital cost breakdown of the site equipment estimated to be required for the ISV of the Weldon Springs site. The equipment listed includes six electrical transformers and six off-gas hoods, with three off-gas treatment systems and three backup blower systems. Each off-gas system and backup blower system would treat the off-gas from two ISV operations, thus reducing capital costs. The equipment costs include the costs for engineering and designing the equipment and mobilizing and demobilizing it at the site. Equipment costs for waste excavation and transport are not included in this itemized list, however. In addition, the equipment costs for filtration of the Weldon Spring sludge have not been estimated.

Site operating costs are listed in Table 9-12. Energy consumption is clearly the single largest item contributing to treatment costs. If equipment costs (from Table 9-11) are added to treatment costs, energy consumption still accounts for 49% of total costs. The costs for the 3 off-gas systems, on the other hand, drops to only 9% of total costs. Clearly, any effects to reduce treatment costs at Welden Spring should be targeted primarily at reducing energy consumption.

Actual methods considered to reduce ISV costs at Welden Springs is included the following:

1. Use three off-gas systems instead of six. This would net a $9 M savings.

2. Dewater the raffinate sludge from 24 wt% solids to 35 wt% solids prior to ISV. By reducing the energy required to vaporize the excess water, as much as $10 M may be saved.

3. Combine contaminated materials prior to treatment. Because the sludge required the addition of soil or clay prior to vitrification, contaminated soil and contaminated clay-liner could be substituted for clean material netting a calculated net savings of $8.8M.

9.3.2 Estimation of Melter Vitrification Costs

The JHCM was also evaluated as a possible remediation process for the Weldon Spring site. In this section cost estimates from this evaluation will be presented. Cost estimates are broken down by capital equipment costs, capital costs, and operating costs. These are described sequentially.

Capital Equipment Costs. The equipment list in Table 9-13 is complete for preparing and vitrifying the wastes. Included in the list are equipment needed for size reduction and blending, vitrification, glass product handling, and off-gas treatment. Not included are equipment associated with excavation of raffinate pit materials. The JHCM represents over 82% of equipment costs by itself.

Capital Costs. Capital costs include capital equipment costs as well as costs in support of capital equipment, etc. These are itemized in Table 9-14. The costs assume that the facility can be built using standard practices for chemical plant structures with additional requirements for ventilation, filtration, and monitoring equipment given that the site contains low-level radioactive wastes. Table 9-14 shows that the melter is the most expensive single capital expenditure, but that purchased-equipment installation and building and facilities also contribute greater than 10% of capital costs.

Table 9-12. ISV Site Operating Costs (Koegler et al., 1989)

Cost Breakdown	Cost, $1000 (% operational cost)	
Labor Costs		
Vitrification Crew	$ 7,380	(10%)
Heavy Equipment	1,480	(2%)
Total Labor	8,860	
Consumable Costs		
Electrodes	21,900	(28%)
Energy	46,100	(60%)
Secondary Waste	439	(0.5%)
Total Consumables	68,500	
Total Operating Costs	$77,400	

Operating Costs. Costs associated with the operation of the vitrification facility include the cost of bulk chemicals added to the feed to improve product quality (borax and soda ash), utilities, and labor. The labor costs include operating personnel for three shifts per day, a plant manager, maintenance personnel, clerical staff, and overheads. It was assumed for this evaluation that the vitrification facility would operate seven days per week, 365 days per year, with an on-line efficiency of 80%. Costs associated with the start-up of the facility were not included but assumed to be insignificant. Electrical costs included as part of the utilities costs are based on an electricity rate of $.06/kWh. Treatment would be completed in about four years at a total operating cost of $60M.

Given these operating parameters the total operating costs break down as follows:

Labor cost	$4.2 M (7% of total costs)
Cost of chemical additives	$21.7 M (36%)
Utilities cost	$34.4 M (57%)

Summary. If equipment costs, costs in support of capital equipment and operating costs are combined. The total remediation cost becomes almost $77M. This breaks down as presented in Table 9-15.

From these comparisons, it can be seen that utilities still are the primary remediation cost, followed by the cost of the chemical additives. Melter costs, the single item dominating capital costs, is only 5.8% ($4.5M) of the total remediation costs.

Costs Reduction. In the process of cost analysis, certain decisions were made to reduce the cost of remediation. Several answers were pursued in these reductions. Examination of these will give some idea of similar reductions that can be made at other sites. Specifically the costs estimated included the following actions:

1. Selection of a fluxing agent based on a compromise between desired processing characteristics and costs. Li_2O or B_2O_3 were mixed with Na_2O and these mixtures were compared as potential fluxing agents. It was estimated that use of the Li_2O mixture would reduce the total quantity of glass produced and the total processing time for the site. However, Li_2O proved to be a more expensive additive (by a 350% increase in additives cost) than B_2O_3 and these costs outweighed the other savings. Therefore, the best

Table 9-13. Equipment Required for JHCM Processing (Koegler et al., 1989)

Equipment	Quantity	Total Cost, $1000
Bulk Materials Handling		
Raffinate Sludge Transfer Pump	2	30
Crush, Delump Unit	1	50
Clay Liner/Vicinity Soil Transfer System	1	25
Chemical Additive Unloading Station	1	50
Chemical Additive Transfer System	3	75
Mechanical Mixer	1	50
Melter Feed Transfer System	1	25
Melter feed Storage Silo	1	20
Melter Feed Transfer System	1	25
Dust Abatement System	1	150
Melter Feed System		
Melter Feed Storage Hopper	1	25
Rotary Valve	1	25
Joule-Heated Ceramic Melter		
Melter	1	4500[a]
Off-Gas Treatment System		
Quench Scrubber	1	50
Scrub Solution Recycle System	1	35
Roughing Filter	1	25
Heat Exchanger	1	25
HEPA Filter	1	15
Concentrator	1	50
Blower	1	150
Glass Handling System		
Glass Quencher	1	50
Heat Exchanger	1	25
Fritted Glass Transfer System	1	25
Total Equipment Cost:		$5,500

[a] Value is total cost of JHCM system including transformers

fluxing agent proved to be a mixture of Na_2O and B_2O_3 in a ratio of 7:1.

2. Blending of waste streams. The waste material to be treated at Weldon Springs consisted of three matrices: sludge, soil, and liner from the sludge pits. Alone, each matrix had chemical composition defects which would require the addition of additives to create a durable glass. However, if mixed prior to vitrification, the blending would remediate some of the deficiencies of each matrix. Additives required and costs would therefore be reduced.

3. Dewatering the sludge. As described in Chapter Seven, dewatering would increase the efficiency of the melter and could prove cost effective by reducing total treatment time.

4. Use of a high-temperature melter. Waste matrices at the Weldon Springs site require a temperature of 1450° C to melt. By permitting a higher operating temperature, a high-temperature melter reduces the need for fluxes. This reduces additive costs and may make the increased cost of a high-temperature melter pay for itself.

5. Fritting the waste glass instead of pouring it into canisters. This option reduces the complexity of waste material handling after vitrification and thus reduces costs. This option is dependent on the quality of the fritted glass product.

Table 9-14. Capital Cost Summary for JHCM (Koegler et al., 1989)

Capital Equipment Costs	Costs ($1000)	% Total Cost
Bulk Materials Handling Equipment	500	3%
Melter Feed System	50	<1%
Joule-Heated Ceramic Melter	4500	28%
Off-Gas Treatment System	350	2%
Glass Handling System	100	<1%
Total Equipment Costs	**$5,500**	34%
Purchased-Equipment Installation	1,800	11%
Instrumentation & Control	850	5%
Process Piping	650	4%
Electrical	1,100	7%
Auxiliaries	1,100	7%
Building & Facilities	2,200	14%
Site Preparation	550	3%
Contingency	1,100	7%
Fees and Engineering Contingency	1,400	9%
Total Costs in Support of Equipment	**$10,750**	66%
Total Capital Costs	**$16,250**	100%

Table 9-15. Comparison of Capital Costs and Operating Costs for a JHCM (Koegler et al., 1989)

Capital Costs	**$16.3M (21%)**
Equipment costs	$5.5M (7%)
Costs in support of capital equipment	$10.8M (14%)
Operating Costs	**$60.3M (79%)**
Labor costs	$4.2M (5%)
Chemical additives cost	$21.7M (28%)
Utilities cost	$34.4M (45%)
Total Cost	**$76.6M**

9.3.3 Additional Cost Factors

Two additional factors play an important role in remediation costs: throughput rate and energy costs.

Throughput rate is the amount of material that can be processed per unit time. High throughput rates generally decrease costs because of economy of scale. Because of the reduction in volume during vitrification, throughput is often expressed both in terms of feed material treated per unit time and glass produced per unit time. Selected throughputs are presented in Table 9-16. The values presented represent process results under a variety of conditions and do not necessarily represent maximum throughput or expected throughput. For example, when using a glass melter to vitrify, process rate can be adjusted by varying the size of the melter. For solutions and concentrated slurries, the process rate is between 36 and 85 gallons/hour/square foot. For contaminated soils and other inorganic feeds, the process rate ranges from 400-600 pounds/day/square foot. Obviously, for increased process rates the melter must be increased in size. In addition to melter size, processing rate will be affected by water content, inherent energy content, particle size, etc.

Energy demands for vitrifying a waste (kwh/ ton of waste or soil) will also vary with a variety of factors, but will depend primarily upon water content and exothermic energy present in the feed.

Table 9-16. Throughput Rates for Selected Vitrification Processes

Melter Type	Feed Type	Feed Input Rate	Glass Production Rate
LFCM - West Valley	HLLW	150 L/h	45 kg/h
AVM - France	calcined HLW	60 L/h	25 kg/h
Glass Melter - Penberthy	toluene, oil	125-1000 lb/h*	500-4000 lb/h*
Glass Melter - Penberthy	spent resins	250-1000 lb/h*	500-4000 lb/h*
Glass Melter - Penberthy	wood, cloth, paper	400-4000 lb/h*	500-4000 lb/h*
coal-fired melter - Vortec	glass-making	20 tons/day	NA
glass melter - Vitrifix	asbestos-contaminanted soil	5 tons/day	NA
rotary kiln - MSP	incinerator ash, soil	100 tons/day	NA
ISV	soil	--	3.5 to 4 tph

*Glass production is greater than feed input due to the need to add substantial glass forming materials to these types of contaminants.

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Appendix A: Summary of Selected Vitrification Tests to Date

Year of Study	Site/Contractor	Waste Feed	Contaminant	Vitrification Process (Vendor)	Scale	Reference
I. Joule-Heated Ceramic Melter						
1975-present	PNL	liquid sludge	HLLW	LFCM	series of tests	Chapman and McElroy, 1989
1977-present	Institute for Nukleare Entosogungstechnick, Karlsruhe, West Germany	liquid sludge	HLLW	LFCM	series of tests	Chapman and McElroy, 1989
1978-present	SRS	liquid sludge	HLLW	LFCM	series of tests	Chapman and McElroy, 1989
1978-present	Power Reactor and Nuclear Fuel Development Corp., Tokai-Mura, Japan	liquid sludge	HLLW	LFCM	series of tests	Chapman and McElroy, 1989
	Ishikawajima-Harima Heavy Industries Co., Yokohama, Japan	liquid sludge	HLLW	LFCM	series of tests	Chapman and McElroy, 1989
1980s	Lohr am Main	asbestos waste	asbestos	glass melter (Sorg)	small- to pilot-scale	Berkey, 1989
1981-present	Eurochemic, Mol, Belgium	liquid sludge	HLLW	LFCM	series of tests	Chapman and McElroy, 1989
1984-present	WVDP	liquid sludge	HLLW	LFCM	series of tests	Chapman and McElroy, 1989
1986	Superfund Wastes	NA	organics and inorganics	electric pyrolyzer (Westinghouse)	pilot	NA
1986-88	Russia	Calcined HLW	HLW	calcination followed by JHCM	operational	Baehr, 1989
1987	Dalzell Glassworks, W.V./ demonstration for EPA	asbestos-contaminated wastes	asbestos	glass melter (Vitrifix)	full	Roberts, 1989
1987	USATHMA	ash from the incineration of paint sludge wastes	organics and inorganics	crucible melts	bench	USATHMA, 1987

Appendix A (continued)

Year of Study	Site/Contractor	Waste Feed	Contaminant	Vitrification Process (Vendor)	Scale	Reference
1988	Faslane Site, England	soil	asbestos	glass melter (Vitrifix)	operational	Denner, Langridge, and Affleck, 1988
1989	Gulfport, Ms./ U.S. Air Force	soil	TCDD and other organics	Advanced Electric Melter (J.M. Huber Co.)	pilot, since shelved	NA
1989	USA/international consortium	asbestos waste	asbestos	glass melter (Sorg)	pilot	Berkey, 1989
1989	Weldon Springs, Mo./DOE	sludge, soil, quarry refuse	TNT, DNT, U, Th, decay products	JHCM	bench	Koegler et al., 1989
1989	vendor	drums	RCRA organics and inorganics	glass melter (Penberthy)	full	vendor
1990	Japan	fly ash	volatile metals	joule-heated melter	pilot	NA
1990	Queensborough, England	contaminated soil	heavy metals & asbestos	glass melter, Dunston Ceramics	NA	Clery, 1990
1991	Fernald, Oh./ DOE	K-65 silo residue	radium, uranium, uranium daughter products, heavy metals (lead)	test crucible	bench	Janke, Chapman, and Vogel, 1991
1991	Whatcom County, Wa./ Recomp of Washington	MSW incinerator ash	inorganics and organics	joule-heated	bench	Chapman, 1991
1991	SRS/DOE	slurry	HLLW	stir-melter (Glasstech)	full (glove-box)	Richards and Lacksomen, 1991
1991	vendor	fiberglass scrap	fiberglass	stir-melter (Glasstech)	full (glove-box)	Richards and Lacksomen, 1991
1991	vendor	municipal waste combustor, fly ash	inorganics	stir-melter	full (glove-box)	Richards and Lacksomen, 1991
present	Himel, Switzerland and Kiel, Germany	fly ash from hazardous waste incineration	heavy metals (W&E Umwelttechnik)	electric melter	operational	Gilges, 1991

Appendix A (continued)

Year of Study	Site/Contractor	Waste Feed	Contaminant	Vitrification Process (Vendor)	Scale	Reference
II. In Situ Vitrification						
1985	EPRI, Wa.	soil	PCBs	ISV	bench	Timmerman, 1986
1987	ORNL, Tn./DOE	seepage pits and trenches	liquid radioactive waste	ISV	pilot	Spalding and Jacobs, 1989
1987	PNL, Wa./DOE	waste crib	mixed	ISV	large	Buelt and Westsik, 1988
1988	New Bedford Harbor Superfund site, N.Y./EPA	sediment	PCBs	ISV	bench	Reimus, 1988
1988-89	AEDC, Tn./ DOE	soil	organics (petroleum products), metals	ISV	feasibility and pilot	Timmerman, 1989 Timmerman and Peterson, 1990
1989	PNL, Wa./DOE	soil from INEL	spiked with steel to test shorting of EFS	ISV	engineering	Farnsworth et al, 1990
1989	PNL, Wa./DOE	UST	radioactive and metal contaminants	ISV	engineering	Campbell et al, 1990
1989	SRS, S.C./DOE	soil	primarily radioactive and metal	ISV	bench	Campbell and Buelt, 1990
1989	Weldon Springs, Mo./ DOE	sludge, soil, quarry refuse	TNT, DNT, U, Th, decay products	ISV	bench	Koegler et al., 1989
1990	Denver Radium Site, Co./ EPA	soil	mixed	ISV	bench	NA
1990	INEL, Idaho/DOE	buried waste	organics, metals, simulated radioactive wastes	ISV	pilot	Callow et al, 1991
1990	NA	sludge and soil	mercury, arsenic, aldrin, and dieldrin	ISV	engineering	Timmons et al., 1990
1990	Northwest Transformer Superfund site, Wa.	soil	PCBs	ISV	engineering	Geosafe, 1991
1991	ORNL, Tn./DOE	waste pits and trenches	radioactive and inorganic contaminants	ISV	pilot	Spalding et al., 1991

Appendix A (continued)

Year of Study	Site/Contractor	Waste Feed	Contaminant	Vitrification Process (Vendor)	Scale	Reference
III. Plasma Heating						
1985-89	vendor-tests/ test run for EPA	soil	15% oil spiked	Plasma Centrifuge Reactor (Retech)	bench to pilot	Eschenbach, Hill, and Sears, 1989
NA	Martiques, France/ vendor	hospital wastes	biological	plasma heating (Aerospatiale)	NA	vendor
1988-89	Glouster, Ontario, Canada/ Ontario Ministries of Energy and Environment, other co-sponsors	MSW	organics & inorganics	plasma arc torch Resorption Canada, Limited	feasibility	Carter et al., 1990
1990	Basel, Switzerland/ MGC, Plasma, Ltd.	drummed waste	organics and inorganics	Plasma Centrifugal Reactor (Retech)	operational	Schlienger and Eschenbach, 1991
1990	Butte, Mont./ DOE/EPA	soil	diesel fuel oil	Plasma Centrifugal Reactor (Retech)	pilot	Viall, Sears, and Eschenbach, 1990
1991	Georgia Tech Construction Research Center, Ga./DOD		asbestos	plasma heating	bench	Associated Press, 1991
present	Hamburg,-Staffenfeld, Germany	fly ash from hazardous waste incineration	inorganics	plasma heating (Krupp Mak GmbH)	pilot plant (1.3 mt/hour)	Gilges, 1991
IV. Microwave Heating						
1988	Japan/Power Reactor and Nuclear Fuel Development Corporation	incinerator ash and liquid sludge	radioactive wastes	microwave (Kobe Steel, Ltd.)	full	Komatsu et al, 1990
1990	Rocky Flats, Colorado, DOE	sludge	TRU	microwave	bench & pilot	Petersen, 1990

Appendix A (continued)

Year of Study	Site/Contractor	Waste Feed	Contaminant	Vitrification Process (Vendor)	Scale	Reference
V. Miscellaneous Electric Heating						
1978-present	Marcoule, France/ CEA	calcined HLW	HLW	calcinatation followed by induction melting	production	Baehr, 1989
1991	Sellafield, England	Calcined HLW	HLW	calcination followed induction melting	operational	*Nuclear Engineering International,* 1990
1992	Albany, Oregon/ BOM	MSW ash, fly ash, ash from sludge incineration	inorganics & organics	electric arc	shakedown	NA
VI. Thermal Process Heating						
1987-present	Louisiana/vendor	incinerator ash and baghouse dust	inorganics and some organics	rotary kiln (Marine Shale Processors)	operational at present	Harlow et al., 1989
1988	Gas Research Institute	fly ash	cadmium and lead	thermal process heating	bench	GRI, 1989
1988	Chiyoda R&D Center, Japan Chyoda Chemical Engineering and Construction Co., Ltd.	simulated waste	combustibles, flame retardants, non-combustible	rotary-kiln	pilot-plant	Wakui et al., 1988
1988-present	Brisbane, Australia	modified MSW	organics & inorganics	modified rotary kiln process/ Nentralysis Industries	30 tonnes/day pilot-plant	NA
1990	vendor/demonstration for EPA	electroplating wastes	lead and other inorganics	kiln (IRI)	full	*The Hazardous Waste Consultant,* 1990a
1990	vendor	hazardous waste dust	lead and other inorganics	Cyclone Melting System (Vortec)	full	Hnat et al., 1990b
1990	Belgium	contaminated soil	NA	furnace, Dunston Ceramics	50 tonnes/day	Clery, 1990
March 1991	Monaca, PA/ SITE	smelter blast furnace soda slag	metals & inorganics	flame reactor, Horsehead, Inc.	demonstration	USEPA, 1991

*U.S. Government Printing Office: 1992 — 648-003/41842