The Storage and Disposal of Radioactive Waste as Glass in Canisters

J. E. Mendel

December 1978

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Richland, Washington 99352

ABSTRACT

A review of the use of waste glass for the immobilization of high-level radioactive waste glass is presented. Typical properties of the canisters used to contain the glass, and the waste glass, are described. Those properties are used to project the stability of canisterized waste glass through interim storage, transportation, and geologic disposal.

FOREWORD

This report is written for a diverse audience, including: 1) members of the public desiring to be better informed about nuclear issues, 2) governmental personnel involved in making decisions relating to waste management, and 3) interested scientists and engineers. Hopefully, aiming at the diverse audience has not detracted from the usefulness of the report, and all will find something worthwhile. The subject is timely. This summer, the first production plant for manufacturing high-level radioactive waste glass in stainless steel canisters, the French AVM plant at Marcoule, became operational. New questions arose concerning whether glass is really the best choice as a waste form for high-level waste.

An executive summary is included at the beginning of the report for those short of time; a comprehensive bibliography is included at the end for those desiring yet more information.

EXECUTIVE SUMMARY

A very satisfactory method for minimizing the hazards associated with the storage, transportation, and final disposal of radioactive waste is to incorporate the waste in glass and place the glass in steel canisters. The waste components become chemically bonded in the glass structure and assume the chemical inertness of the glass itself. The chemical inertness of glass insures against deleterious reactions between the waste glass and its canister. The glass-canister combinations thus form excellent packages, or capsules, for convenient, safe handling of highly radioactive waste. These capsules are reliable for storage, transportation, and final disposal in deep geologic repositories located in specially selected salt, shale, or crystalline rock formations.

**THE TECHNOLOGY FOR
INCORPORATION OF
RADIOACTIVE WASTE IN GLASS
IS AVAILABLE.**

Waste vitrification processes for production of the glass-canister capsules are available; characteristics of the capsules, particularly as they relate to long-term behavior have been studied extensively and more studies are being made. The studies show conclusively the viability of glass as a long-lived waste form. The continuing studies will refine waste management parameters in greater detail and define more accurately any limits which should be placed on operating, handling, and storage conditions.

**GLASS READILY
INCORPORATES THE COMPLEX
MIXTURE OF FISSION PRODUCTS
AND ACTINIDES THAT ARE
IN HIGH-LEVEL WASTE.**

Waste glasses have three special features: 1) they are more complex chemically than commercial glasses, 2) they will self-heat for hundreds of years, and 3) they will self-irradiate for hundreds of thousands of years. Detailed studies have shown that glass, as a class of material, readily accommodates these special features.

Worldwide, thousands of waste glass formulations have been prepared, demonstrating again and again the innate ability of glass to readily incorporate the 30 to 50 elements often present in radioactive waste. These waste elements usually constitute 25 to 35% of the weight of the waste glass.

Laboratory and pilot plant studies have demonstrated that glass has good high-temperature stability and outstanding radiation stability. The stability has been demonstrated to be sufficient for incorporation of the most radioactive high-level wastes from reprocessing light-water power reactor fuel or breeder reactor fuel. However, near-term application of waste glass is only for wastes from low exposure fuel from the defense program or aged power reactor fuel.^(a) Thus, the first full-scale applications will produce glass canisters with relatively low self-heating and self-radiation levels, a fittingly conservative method of introducing new technology.

Temperatures in the waste glass canisters are regulated by control of such variables as contained radioactivity, canister diameter, and the distance between canisters in a storage array. After the glass solidifies in the canister, the wall temperature is maintained at less than 375°C, a temperature at which the glass is stable. Interior temperatures may be higher, however, due to radioactive self-heating, and there may be some devitrification of the glass along the centerline of the canister. Devitrification is the spontaneous formation of scattered microscopic crystals in the glass matrix. The crystals, usually containing only two to three components, form more thermodynamically stable configurations for their special components than does the original glass. Devitrification is

**INTERIOR PORTIONS OF HIGHEST-
HEAT PRODUCING GLASS
CANISTERS MAY DEVITRIFY;
THE EFFECTS ARE MINOR.**

(a) The AVM, the world's first industrial-scale nuclear waste vitrification plant, which went into radioactive operation in 1978 at Marcoule in France, will initially process wastes from aged fuel and will never process wastes from fuel with more than 5000 MWd/MT exposure. The French plan to install another waste vitrification plant at La Hague in the early 1980s which will convert wastes from more highly irradiated nuclear power plant fuel into glass.

a time- and temperature-dependent phenomenon occurring in all glasses. In waste glasses, it occurs at measurable rates between 500 and 950°C. The near-term effects of devitrification are well understood and for borosilicate waste glasses consist mainly of an increase in leach rate. The increase is usually only a factor of two to three and has never been observed to be more than a factor of 10. Waste glass compositions can be controlled so that devitrification does not affect their coherence and strength.

Radiation effects on waste glasses have been studied extensively and found to be minor. The studies have emphasized the actinides, since their radioactive decay produces the alpha and alpha-recoil particles which have the most potential for causing radiation effects in waste glass. The principal radiation effects saturate at harmless equilibrium values after cumulative doses of less than 5×10^{18} alpha events per g of glass. The principal effects are buildup of stored energy (maximum = 60 cal/g) and a change in density (maximum = 1%). Preliminary testing of waste glass with saturated radiation effects shows no changes in impact strength or leach rate. The conclusions of the radiation effects studies are that waste glasses can safely incorporate at least 1×10^5 Ci of beta-gamma-active isotopes and 1×10^3 Ci of alpha-active isotopes per L, and probably much more.

**GLASS EXHIBITS OUTSTANDING
RADIATION STABILITY.**

The objective in making waste glass is to provide protection against dispersion of radioactivity into the biosphere. During all steps of the waste management system, primary reliance is placed on redundant barriers external to the waste glass. The primary barrier during interim storage and transportation is the canister, but other additional barriers are always present. The waste glass furnishes an inert final barrier in the extremely unlikely event all other barriers fail. If the other barriers do fail, for whatever reason, there are three mechanisms by which activity can be released from the waste glass: high-temperature vaporization, dispersion by air-borne particulates, and dispersion by water that has dissolved small amounts of the glass. All of these release mechanisms have been studied extensively, and the studies are continuing. Based on

**REDUNDANT BARRIERS ARE
FEATURED IN WASTE
MANAGEMENT SYSTEM.**

the data already obtained, it is possible to predict the amount of activity that would be released under any given conditions, if the conditions are defined in enough detail.

The conditions of interest during interim storage and transportation are the elevated temperatures or high impact conditions which could occur in a severe accident--it is only in such accident situations that the properties of waste glass come into play as the final barrier to radioactivity release.

The formation of vapors which could unduly pressurize the canisters is prevented because the temperatures of waste glass manufacture, 950 to 1150°C, are higher than the temperatures of any credible accident. The sources of potential volatiles, such as nitrates, are removed during glass manufacture. Only a few radioactive isotopes are volatile to a measurable extent, even at waste manufacturing temperatures. The temperature dependence of these volatilities is known for selected waste glasses. Their volatilities can be extrapolated to lower temperatures for analyses of postulated accidents in which the canister is breached and bare glass is exposed to elevated temperatures, in a fire, for instance.

The dispersion of glass particulates from a canister of waste glass is almost inconceivable. Simulated waste glass canisters have been subjected to the same impact tests that are specified by the Department of Transportation (DOT) to qualify casks for the shipment of highly radioactive material. The canisters were not breached. Canisterized waste glass will be transported inside heavily shielded casks, so during shipment the waste will be within two containments, both of which have passed the DOT impact tests. The fraction of the glass in a canister that is converted to respirable-sized particles (less than 10 μ m in dia) has been measured at different impact velocities. The fraction is approximately 0.01% at 117 ft/sec, equivalent to an 80 mph crash with no cask or other shock absorbing material present. The tests also showed that, even in the extreme high impacts, all of the particles were contained in the canister.

**STEEL CANISTERS ARE PRIMARY
BARRIER DURING ABOVE-
GROUND STORAGE AND
TRANSPORTATION OF WASTE.**

From the above discussion, it may be concluded that failure of the canisters while they are in interim storage or being transported, either due to internal pressurization or external impact, is extremely unlikely, even during severe accidents. In summary, while canisterized waste glass is above ground in man's biosphere, the canisters will effectively prevent release of the contained activity, and the backup inert properties of the glass will rarely, if ever, be needed. If an accident does occur during interim storage or transportation it will usually affect only individual canisters and never more than a small number; the radioactive inventory involved will be relatively small. The largest inventories of waste glass capsules accumulate at the final disposal sites.

Final disposal of the waste glass capsules is planned to be by isolation underground in deep geologic repositories 2000 ft or more below the surface. Current regulations require only that the canisters maintain their integrity for 90 days after emplacement in the repository, but these regulations are being re-evaluated. The capsules may be engineered, through overpacks or other features, to have a longer minimum life in the repositories. Reasons for engineering a longer lifetime include: 1) to allow relatively easy retrieval for a predetermined period, or 2) to permit decay of ^{90}Sr , the isotope initially present in the most hazardous concentrations. Representative lifetimes required for these purposes might be 50 and 500 yr, respectively, although final decisions in this area have not yet been made. In any event, the design lifetime of the canister and other outer barriers that may be placed around the waste glass will be shorter than the life of some of the radioisotopes contained in the glass. It is accepted that at some time, as these other parts of the capsule gradually deteriorate, at least some portions of the waste glass with its residual radioisotopes may be exposed to water, if it is present in the repository. The low leach rate of waste glass will then become one of the barriers to escape of radioactivity from the repository.

**FINAL DISPOSAL WILL BE IN DEEP,
STABLE GEOLOGIC FORMATIONS;
NATURAL RETENTION OF RADIO-
ISOTOPES IN SOIL IS ADDITIONAL
ASSURANCE OF ISOLATION.**

**WASTE GLASS PROVIDES
BACKUP BARRIER IN GEOLOGIC
REPOSITORIES.**

The chemical durability of waste glass will provide backup protection in the repository, just as it does in surface accidents. The primary protection lies in the isolation of the repository from the biosphere furnished by: 1) intervening impervious geologic formations, which assure a tortuous, lengthy path for any water reaching the biosphere from the repository, and 2) the ion exchange and adsorption characteristics of the 2000+ ft of overburden, which act to cleanse the water of radioactivity. The net long-term (millenniums) effect may be thought of as a gradual, probably horizontal, enlargement in the size of the repository, with its boundaries becoming slowly more diffuse. At the Oklo natural reactor site, about 6 tons of fission products and 3 tons of plutonium were, in a sense, deposited in a geologic repository 1.9 billion yr ago. Analysis of this site shows that, at least for one specific geology, the increase in effective repository size was minimal for the long-lived actinides.^(a) The role of waste glass in the repository remains of interest, however, because its stability can act as a throttle on the release of activity to any water present. Considerable experimentation has recently started to increase understanding of waste glass/water/geologic host interactions.

Two major types of geologic repositories are being considered, those located in salt formations and those located in nonsalt formations, such as basalt, granite, and shale. The probable conditions of waste glass exposure to water differ for the two repository types. In salt repositories the exposure will be to a small amount of stagnant saturated salt brine in an essentially sealed system. In nonsalt repositories the exposure will be to varying amounts of groundwater which may slowly migrate to and from the repositories through fissures, cracks, and porosity in the geology.

(a) When the earth was considerably younger, a natural nuclear reactor was created in what is now West Africa at Oklo in a rich uranium deposit. The site was discovered in 1972 and since then the isotopic abundance of fission product and actinide elements in the vicinity has been studied exhaustively. The evidence is that except for Cs, Rb, Sr, and Ba, all of the radioactive products of the reactor have stayed at their point of origin, even though 1.9 billion yr have elapsed.

**WASTE GLASS-BRINE REACTION
PRODUCTS WILL BE LOCKED IN
SALT REPOSITORY.**

Salt formations demonstrate by their very existence that they are low water-content systems. Otherwise they would have dissolved and dispersed long ago. Their obvious freedom from water was one of the reasons leading to the selection of salt formations as foremost candidates for siting geologic repositories. There is a small amount of water in the salt, however, a relic of the final stages of the seawater evaporation that formed the salt formations. Some of this water will tend to collect around the canisters and, after the repository is sealed, may reach temperatures of 150°C and 2000 psi pressure, depending on the design conditions selected for the repository. (The design conditions which should be used are still being evaluated and may ultimately limit the maximum temperature to below this value.) The maximum temperature occurs in the first few decades of repository life. Then the temperature decreases as ⁹⁰Sr and ¹³⁷Cs, the major heat producers, decay with 30-yr half lives. Tests show that the rate of attack on the waste glass at 150°C is 100 to 500 times that at 25°C. Tests also indicate that in a closed system with limited water, an apparent steady state is reached rapidly. At steady state, a layer on the waste glass surface will be altered; the potential surface reactions are complex and are only beginning to be defined. Some of the glass in contact with salt brine will be converted to crystalline forms at temperatures as low as 150°C; some of the constituents from the waste glass, cesium for instance, will simply dissolve in the salt brine. The end result will be a small amount (no more than 4 to 8 gal) of contaminated brine in the vicinity of each waste capsule, surrounded by many feet of stable salt formation in all directions.

Nonsalt repositories will probably be wetter than salt repositories. Various cracks and pores will provide pathways for the ingress and egress of water. The rates of water flow can be estimated to be low but cannot be known precisely. Thus water which has leached radioactivity from the waste glass can potentially migrate from the repository. The distance the

**WASTE GLASS-GEOLOGY
REACTION PRODUCTS CAN
POTENTIALLY MIGRATE SLOWLY
FROM NON-SALT REPOSITORIES.**

radioisotopes migrate before they decay to nonradioactive isotopes, or reach the biosphere, depends not only on the amount leached from the waste glass, but also on the flowrate of the soil water and the retention capacity of the geologic formation the water passes through. Soils have a very high retention capacity for actinides and most fission products. Computer modeling of migration from nonsalt repositories shows very low releases to the biosphere, but the models must still be refined. Part of the refinement will be to better define the probable release rates of activity from waste glass to water in the repository.

The amount of radioactivity leached from the glass will depend on many factors, but the most important parameter is temperature. If the temperature of the water is 100°C, the amount of activity leached will be 10 to 50 times that leached at 25°C; if the temperature is 150°C, the amount of radioactivity leached will be approximately 100 to 500 times that leached at 25°C. Also, at about 150°C, complex hydrothermal alteration reactions begin to occur at measurable rates. Study of these high-temperature reactions is just beginning. There is already good understanding of the leach behavior of waste glass below 100°C--it is only above 100°C that detailed information is not available.

**CAUTIOUS APPROACH IS TO
LIMIT WASTE GLASS-GEOLOGY
REACTIONS BY TEMPERATURE
CONTROL UNTIL MORE STUDIES
ARE MADE.**

A systems approach to waste management is being used. This includes taking account of the state of knowledge concerning each component in the system. Even though waste glass is only a backup barrier in the system, a prudent and practical way to begin operation of nonsalt repositories will be to limit the operating temperature to below 100°C. Several ways of accomplishing this are discussed in the main report. There will be an ipso facto temperature limit since the first wastes to be placed in geologic repositories will be low-heat defense wastes and long-cooled commercial wastes. Thus, there will be plenty of time to research the high temperature leach reactions and refine the migration model. The cost-saving benefits of higher repository heat loadings can be evaluated when these studies are completed.

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1

INTRODUCTION

THE TECHNOLOGY EXISTS TO IMMOBILIZE
RADIOACTIVE WASTE IN GLASS

2

FORMATION OF RADIOACTIVE WASTE
GLASS

3

PROPERTIES OF RADIOACTIVE WASTE
GLASS IN CANISTERS

4

STABILITY OF CANISTERIZED RADIOACTIVE
WASTE GLASS DURING HANDLING,
STORAGE AND FINAL ISOLATION

a. OPERATING (RIGHT) AND STORAGE (LEFT) FACILITIES

b. CONTROL ROOM

FIGURE 1. The AVM Plant for Production of Waste Glass, Marcoule, France

1.0 INTRODUCTION

Glass has long been recognized as a promising medium for immobilization of the fission product, actinide, and actinide daughter activity in radioactive wastes. Laboratory development of glass compositions for incorporation of the high-level waste (HLW) started about the same time the first commercial nuclear power was generated, over 20 yr ago (White, 1955; Goldman, 1958; Watson, 1958). Development of processes which could reliably produce the waste glasses, while being operated remotely behind heavy shielding, began shortly thereafter. Radioactive pilot plant demonstrations of HLW vitrification were conducted during the 1960s in England (Grover, 1966), France (Bonniaud, 1973), and the U.S. (McElroy, 1972). The latter two demonstrations in particular involved exhaustive testing which extended over several years. About 15,000 kg of borosilicate glass containing 5,000,000 Ci was produced in the French pilot plant. Over 2200 kg of phosphate and borosilicate glass containing over 24,000,000 Ci was produced in the U.S. pilot plant. In addition, 1900 kg of a melt-formed phosphate ceramic product containing about 21,000,000 Ci was produced in the U.S. pilot plant.

These pilot plant tests confirmed that waste vitrification processes can be operated remotely behind the heavy shielding of radioactive cells. As a result, the French have installed a plant, the AVM, for vitrification of HLW from the Marcoule reprocessing plant. The AVM, shown in Figure 1, began routine operation in July 1978 and will have converted all of the high-level liquid waste at Marcoule to glass in 10 yr. Preparations are being made to vitrify HLW at the La Hague Reprocessing Plant in France, at the Tarapur Reprocessing Plant in India, at the Eurochemic Reprocessing Facility in Belgium, at the Windscale Reprocessing Plant in England, at the Tokai-Mura Reprocessing Plant in Japan, and at the German reprocessing plant to be constructed at Gorle-

ben (IAEA, 1977). A demonstration of commercial waste vitrification, the Nuclear Waste Vitrification Project, will be completed at PNL in 1979.

Recently, the U.S. decided to develop vitrification processes for the defense wastes at Savannah River, Hanford, and the Idaho Nuclear Engineering Laboratory for possible implementation in the late 1980s. The defense wastes are very heterogeneous. Even after the pretreatments, which are being devised to concentrate the activity in smaller volumes, several different waste glass compositions will probably be required to accommodate the heterogeneity. The properties of these waste glasses, however, will be similar to the waste glasses that have been developed for nuclear power high-level wastes.

Glass is also a promising method for immobilization of nonhigh-level waste containing long-lived radioactivity. For example, combustible waste can be incinerated to achieve a volume reduction of 10 to 50; the resulting ash, containing fine particulates, can then be consolidated in glass.

The benefits of vitrifying radioactive waste are many. First, glass is compatible with the sequential barrier approach that is the cornerstone of our radioactive waste management. Glass can be placed in sealed metal canisters without danger of corrosion or pressurization of the canisters. The sealed canisters, which may be encased in a second metal container, are always within other barriers, such as thick-walled concrete cells, deep water basins, heavily shielded shipping casks, or in specially-selected geologic formations under two or three thousand feet of overburden. High waste loading can be achieved in glass, making it a relatively economic inner core material for the sequential barrier approach to radioactive waste management. Glass gives desirable processing flexibility since a wide

variety of components can be incorporated in varying ratios without adverse effects on properties of the inner core.

The glass actually increases the mechanical strength and deformation resistance of the waste canister in an accident involving impact. In the highly unlikely event a canister is breached in an accident, the exposed glass, because of its chemical inertness, high temperature stability, and resistance to fragmentation into aerosol-sized particles, forms a final barrier to release of the contained radioactivity to man.

This report is designed to describe what radioactive glass is, to describe what its properties are, and especially to describe how it may be expected to behave during storage and disposal. It should be emphasized that, even after waste vitrification process equipment is in place and the process is operating, it will be possible to make changes in glass composition. For this reason the development of waste glasses is still in a dynamic state and may be expected to remain so for some time to come.

1

INTRODUCTION

2

FORMATION OF RADIOACTIVE WASTE GLASS

FORMULATION AND MANUFACTURING TECHNIQUES
CAN BE CONTROLLED TO YIELD DESIRED PROPERTIES
IN RADIOACTIVE WASTE GLASS PRODUCTS

3

PROPERTIES OF RADIOACTIVE WASTE GLASS IN CANISTERS

4

STABILITY OF CANISTERIZED RADIOACTIVE WASTE GLASS DURING HANDLING, STORAGE AND FINAL ISOLATION

FIGURE 2. Spray Calciner In-Can Melter Installation in PNL Nonradioactive Pilot Plant

2.0 FORMATION OF RADIOACTIVE WASTE GLASS

Radioactive waste glasses are formulated by combining a selected mixture of glass formers, modifiers, and intermediates (called the glass-making additives) with the waste. The glass-making additive combination selected depends on the composition of waste being vitrified and on the properties desired in the waste glass. The glass-making additives usually comprise 65 to 85 wt% of the product waste glass. Because of the many different potential formulations possible, waste glass cannot be thought of as a single substance with set properties. It is possible, however, to consider waste glass as belonging to just a few general types, whose properties have a generic similarity, notwithstanding the compositional variations.

The composition selected for a given radioactive waste glass is governed by three factors:

- the constituents of the radioactive waste to be immobilized
- the vitrification process to be used for the immobilization
- the properties desired for the immobilized waste product, i.e., the physical and chemical characteristics desired for the waste glass that is transported away from the processing plants to be placed in geologic disposal.

These factors have been taken into account in the waste glass formulations which have been developed and which will be described in this report.

A wide range of radioactive wastes are candidates for immobilization as glasses. For this reason, the innate flexibility of glass is a definite advantage. It permits a large number of components to be accommodated in varying concentration ratios.

The major formulation requirement imposed by the vitrification process is that the viscosity of the glass be less than a specified value at the processing temperature. Descriptions of radioactive vitrification processes are beyond the scope of this report. A number of waste vitrification processes are well developed and described in detail in the literature (ERDA 76-43). A pilot plant installation of one such U.S. waste vitrification process, the spray calcination/in-can melting process developed at PNL, is shown in Figure 2. The well developed processes have one common characteristic. They all operate at what, for the commercial glass industry, is a very low temperature, 950°C to 1150°C. The viscosity of the glass melt is formulated to be less than 200 poises at the operating temperature. The processes can impose certain additional requirements on the glass, for instance, if the process utilizes joule-heating by passage of electric current through the molten glass, then electrical conductivity versus viscosity relationships become important. Other process-related considerations include high-temperature volatility, corrosion, and melt homogeneity.

Of the three factors listed at the beginning of this section, the most difficult to define is the third. There is general agreement that the properties of the immobilized waste should form an ultimate barrier to release of the contained radioactivity. Throughout the waste management sequence, however, the inertness of waste glass is just the innermost of a sequence of barriers which are engineered into each waste management step. The inertness of the glass is a backup safety precaution which does not come into play at all until the other barriers have failed to perform as they are designed. Presently, criteria for solidified high-level waste in the U.S. date from 1970 and

are contained in 10 CFR 50, Appendix F. They were directed mainly toward assuring the integrity of the next farther-out barrier, the canister containing the solidified HLLW. These criteria state:

"The dry solid shall be chemically, thermally, and radiolytically stable to the extent that the equilibrium pressure in the sealed container will not exceed the safe operating pressure for that container during the period from canning through a minimum of 90 days after receipt (transfer of physical custody) at the Federal repository."

Recently the Nuclear Regulatory Commission (NRC) has begun updating the criteria. A preliminary draft of "Determination of Performance Criteria for High-Level Solidified Nuclear Waste," was released in 1977 (Cohen, 1977). The NRC is continuing to refine and quantify criteria within guidelines being developed by the Environmental Protection Agency (EPA).

2.1 GLASS FORMULATION

Glass formulation is the process in which suitable additives are selected to be added to the radioactive waste in the vitrification process, so that the resulting glass will have properties compatible with both processing and ultimate solidified product requirements. The considerations involved in selection of the glass-forming additives are described in this section.

2.1.1 Elements Which Must be Incorporated in Radioactive Waste Glasses

Glass waste forms were originally developed to immobilize high-level liquid waste (HLLW) resulting from reprocessing spent fuel from nuclear reactors. HLLW has been defined as "... those aqueous wastes resulting from the operation of the first cycle solvent extraction system or equivalent, and the concentrated wastes from subsequent extraction cycles, or equivalent, in a facility for reprocessing irradiated reactor fuels" (10 CFR 50, Appendix F). Today irradiated fuels are reprocessed almost exclusively by the Purex solvent extraction process.

High-level liquid waste usually contains over 99.9% of the nonvolatile fission products and actinides except uranium and plutonium. Uranium and plutonium are recovered during reprocessing for further uses. But due to processing waste losses,

about 0.05 to 1% of the uranium and plutonium in the initial fuel also ends up in the HLLW. Computer programs are available which accurately calculate fission product and actinide concentrations in HLLW as a function of decay time. There are a large number of constituents in the waste due just to fission products, actinides, and their daughters (see Figure 3). However, waste glass formulation would be relatively straightforward if these were the only HLLW constituents. The waste composition would be a known constant except for small perturbations in the fission product spectrum due to variations in initial fuel makeup and nuclear power plant operation, and small variations in day-to-day reprocessing plant losses of uranium and plutonium, (and thorium, if the fuel contained thorium).

As shown in Figure 3, HLLW also contains other constituents in addition to fission products and actinides. These constituents, often referred to as the inerts, account for the diversity in HLLW compositions. They include corrosion products, process additives, and possible other waste streams added to the HLLW because it is a convenient disposal route for wastes containing actinide activity. The inerts usually make up less than 50 wt% of the nuclear power HLLW constituents; they may make up more than 99 wt% of defense HLLW constituents. This is the reason defense HLLW has a much lower heat generation rate than nuclear power HLLW.

2.1.2 Waste Loading Considerations

The variable that exerts the most control over the properties of waste glass is waste loading. Waste loading, expressed as wt%, is the weight proportion of the glass that is waste components, as oxides, versus the overall weight of the glass, which includes the glass formers and modifiers added to produce desired properties in the product material. Obviously, by decreasing the waste loading sufficiently, the concentration of radioactive atoms could be diluted until those atoms were only inconsequential contaminants, without effect on the parent material. Glass compositions of known durability taken from nature, such as rhyolitic obsidian (Washington, 1917) and tektites (O'Keefe, 1976) which have survived in many environments for millions of years, could then be adopted as the model for nuclear waste disposal in glass. However, the question of when the waste ceases to be an inconsequential contaminant, and when a new material has actually been formed, is difficult to answer. Testing would be required

of many waste components in SiO_2 . Although only limited investigations have been made, waste loading is probably restricted to less than 5 to 15% in high-melting glasses.

2.1.3 Structure of Radioactive Waste Glass

Glass is defined as, "... an inorganic product of fusion which has been cooled to a rigid condition without crystallizing" (ASTM). Radioactive waste glass fits this definition quite well. As will be described later, there are usually a few scattered crystals (<5 vol%) present in most waste glasses. However, as a first approximation waste glass is free of crystallization. It is this lack of crystallization which make glasses unique as a class of material.

The difference between glass and crystalline materials is diagrammed in Figure 4. As a crystalline material is cooled in the molten state, it solidifies uniformly at one temperature, shown as line aa in Figure 4. If super-cooling occurs, the temperature of solidification will be somewhat lower. But when solidification is initiated, it still goes to completion at one temperature, as shown in line bb. In contrast, as a glass material is cooled it gradually becomes more viscous. At a viscosity of about 10^{13} poise the change from a super cooled liquid to glass occurs. The temperature at which this occurs is known as the glass transition temperature (T_g). Above T_g the glass is plastic; below T_g the glass is brittle. The exact value of T_g depends on the rate of cooling, being lower for a slower rate of cooling. Thus in Figure 4, $(T_g)_1$ would result from a slower rate of cooling than $(T_g)_2$. Slower rates of cooling in the range of the glass transition temperature are said to "stabilize" the glass, and, as shown in Figure 4, result in a denser glass. Glass is always less dense than a crystalline material of the same composition because in glass the atoms are arranged in a random fashion rather than being locked in a symmetrical array as they are in crystalline materials.

Glasses are metastable. That is, at certain temperatures formation of crystals of fixed stoichiometry can occur spontaneously. This spontaneous crystallization, called devitrification, occurs most rapidly at temperatures 100 to 300°C above the glass transition point. At lower temperatures the kinetics of devitrification become very sluggish, thus natural materials in the glassy state, although

FIGURE 4. Volume-Temperature Relationships for Glasses, Liquids, Super-Cooled Liquids, and Crystals

not in their most thermodynamically stable state, have survived for many millions of years on earth.

Glasses are nonstoichiometric materials, which is a distinct advantage when they are being used to immobilize wastes of indefinite and variable composition. A large amount of work has been done to elucidate the atomic structure of glasses. No one structural theory has gained universal acceptance and it appears likely more than one structural theory will always be required to explain all of the observations (Tooley, 1974). There is general agreement, however, that glass has some short range order over distances of 10 to 20 Å. Beyond this distance order is lost. The term "random network" is often used to describe glass structure.

It is empirically observed that different elements have different effects when incorporated in glass. One theory is that the variation in effects is due to bond strength. According to this theory, the elements can be divided into glass formers, intermediates, and modifiers based on their bond strength. Table 1 lists the bond strengths of some of the oxides found in radioactive waste, plus others. (Sun, 1947). The glass formers alone can form a three-dimensional, random network. The

TABLE 1. Bond Strength of Oxides

	M in MO	Valence	Coordination Number	Single-Bond Strength kcal/mole
Glass Formers	B	3	3	119
	Si	4	4	106
	Al	3	4	107-79
	B	3	4	89
	P	5	4	111-88
	Sb	5	4	85-68
	Zr	4	6	81
Intermediates	Ti	4	6	73
	Zn	2	2	72
	Pb	2	2	73
	Al	3	6	67-53
	Th	4	8	64
	Zr	4	8	61
	Cd	2	2	60
Modifiers	La	3	7	58
	Y	3	6	50
	Sn	4	6	46
	Th	4	12	43
	Pb	4	6	39
	Mg	2	6	37
	Li	1	4	36
	Pb	2	4	36
	Zn	2	4	36
	Ba	2	8	33
	Ca	2	8	32
	Sr	2	8	32
	Cd	2	4	30
	Na	1	6	20
	Co	2	6	20
	K	1	9	13
	Rb	1	10	12
	Cs	1	12	10

oxides of silicon, boron, and phosphorus are the principle inorganic glass formers. Random networks established by these glass formers are the "backbone" of glasses. The network structures tend to be covalently bonded. Modifiers (Table 1) tend to bond ionically to the anions in the glassy network. They are used to alter properties, e.g., the addition of modifiers can decrease viscosity and increase both electrical conductivity and thermal expansion coefficients. An intermediate, although not usually capable of forming a glass, can enter in a glass-forming position and/or a modifying position and thus can help stabilize the glass while also changing its properties. From Figure 3 and Table 1 it can be seen that almost all radioactive waste constituents can have a place in the glass structure, as a modifier, intermediate, or glass former.

There are two conclusions to be drawn from the preceding discussion. First, the structure of glass permits the individual atoms of the radioactive waste to become a coherent part of the glassy structure. The waste is not just encapsulated in glass; each waste atom is separately bound in the glass structure by a chemical bond. (There are certain minor exceptions to this statement, e.g., ruthenium and palladium remain as discrete particles encapsulated in the glassy matrix.) Second, while there are certain guidelines which can be used in glass formation (Rawson, 1967; Bacola, 1972; Heimerl, 1971; Grover, 1960), basically it is an empirical process because of the nonstoichiometric character of glass. It is even possible to make glasses that are deficient in glass formers. Invert glasses do not contain enough silica to provide a continuous

spatial network of SiO_2 tetrahedra, yet they are true glasses (Trap, 1960).

2.1.4 Types of Radioactive Waste Glass

Waste glasses are most conveniently categorized according to the preponderant glass-forming oxide used in the formulation. Silica is the most commonly used glass-former in industry and also in waste glasses. Different types of silica-based waste glasses are described in the next three sections. Phosphate glasses are described in the fourth section. Glasses in which borate is the primary glass former are too water soluble for consideration, but borate in lesser concentrations acts as a valuable fluxing agent in waste glass formulations. Table 2 lists typical compositional ranges for components in the most important waste glass types.

Borosilicate Waste Glasses

Throughout the world, most of the radioactive waste glasses that are developed to the point of process application are borosilicate formulations (IAEA, 1976; IAEA, 1977). Borosilicate glass has long been used industrially and com-

mercially. Pyrex (82% SiO_2 , 12% B_2O_3 , 4% Na_2O) is a borosilicate glass, although, as can be seen by comparison with Table 2, it has quite a different composition from typical borosilicate waste glasses. Boron serves two major and desirable purposes in borosilicate waste glasses: 1) it lowers viscosity and hence processing temperature, and 2) it increases the solubility of many waste constituents in silica-based glass. For these reasons most waste glasses, as shown in Table 2, contain from 5 to 15% wt% B_2O_3 .

There are few potential problems in using boron in waste glass and they are relatively insignificant. In some processes, it is desirable to mix the glass-making additives with the liquid waste prior to vitrification. When this is done, a flocculent precipitate of boric acid may occur and care must be taken to assure that boron is homogeneously distributed in the feed to the vitrification process. Liquid-liquid phase separation occurs in borosilicate glasses of certain compositions. This phenomenon is described in more detail in Section 3.3.2. Its effect on important borosilicate waste glass properties is not measurable.

TABLE 2. Typical Waste Glass Compositions

Oxide	Glass Composition, Wt%			
	Borosilicate	Alumina Silicate	Glass-Ceramic	Phosphate
SiO_2	25-50	33-40	32-60	0-6
B_2O_3	9-22		1-11	
P_2O_5	0-2			30-55
Alkali metal oxides	8-19	18-22	0-13	5-25
Alkaline earth oxides	0-6	13-16	2-33	
Fe_2O_3 , Cr_2O_3 , NiO	1-20			0-30
Al_2O_3	0-10	26-30	10-24	0-35
TiO_2	0-3		0-3	
ZnO	0-22		0-13	
CuO	0-3			
PbO	0-50			0-30
Sb_2O_3	0-12			
Fission products	30	5	20	30
Actinides	10	1	7	10

Alumino-Silicate Waste Glasses

Some of the first waste glass formulations investigated were of the alumino-silicate type (Goldman, 1958). Of particular interest is the Canadian nepheline syenite glass (Table 2). Blocks of this glass were prepared in 1960 and buried a few feet below ground level as bare glass in a swampy area on the Chalk River Atomic Energy Establishment. Leaching of ^{90}Sr from these alumino-silicate glass blocks has been monitored by removing water from nearby test holes (Merritt, 1964). By 1968 the leach rate had reached a steady-state value of 5×10^{-11} g of glass/cm²-day, a very low rate (Merritt, 1977).

An apparent advantage of alumino-silicate waste glasses is excellent chemical durability. There are several reasons why in recent years development of waste glasses has gone in other directions, however:

- The process used to make the Canadian glass was a slow batch process, not easily convertible to use in a high capacity modern plant.
- High glass melting temperatures (1350°C) were required. At these temperatures, even if the newer continuous waste vitrification processes using ceramic melters could be adapted, there would be increased volatility perhaps requiring extra scrubbers in the off gas. Cesium and ruthenium process volatility losses amounted to 30 and 15%, respectively, in the Canadian runs.
- Waste loading is limited. While a large amount of alumino-silicate glass formulation has not been done, indications are fission product oxide loading is limited to less than 10 wt%.

Glass-Ceramic Waste Glasses

Glass-ceramics is a new class of materials which have achieved industrial prominence only in the last 20 yr (McMillan, 1964). Glass-ceramics generally are tougher and have better high temperature stability than regular glasses. They are being used for the new smooth stove tops, for example.

Glass-ceramics are formed by special thermal treatment of glass pieces produced by standard glass manufacturing techniques. The thermal treatment consists of three essential steps. First, the glass pieces are cooled rapidly to prevent crys-

tallization. (The glasses are formulated with a tendency to crystallize--the object is to allow the glass to crystallize, but only under controlled conditions.) Next, the glass pieces are held a few hours at the nucleation temperature, usually around 600°C. This is the key to glass-ceramic production. A very large number of crystal-nucleating sites are formed homogeneously throughout the glass pieces. As the final step the pieces are heated to the crystallization temperature, often about 900°C, where rapid crystallization occurs. Commercial glass-ceramics usually contain over 95 vol% small (<10 μm) uniformly-sized crystals embedded in about 5 vol% residual glass phase. It is the small size and uniformity of the crystals, plus the potential of tailoring the formulation to yield crystals with desirable properties, e.g., spodumene with an almost zero thermal expansion coefficient, that give commercial glass-ceramics their desirable properties.

There has been a modest effort to produce glass-ceramic waste glasses, particularly in Germany (De, 1976; De, 1977). As can be seen in Table 2, silica-based formulations are being used. The incentive is that glass-ceramics is a method of helping assure long-term thermal stability, since the initial waste form would be in its most thermodynamically stable form. (In contrast, regular glass is in a state of kinetic rather than thermodynamic equilibrium.) To date only about 50 vol% crystallinity has been achieved in the glass-ceramic waste glasses. There has been some improvement in toughness and thermal conductivity.

Some of the yet unresolved questions concerning glass-ceramics as a waste form include:

- Can glass formulations be found which permit uniform and complete crystallization of all of the radioactive constituents?
- Will the residual glassy phase have sufficient chemical durability if contacted by water to continue to bind the crystals together in a massive low-surface area configuration?
- Can the temperature program required to produce glass-ceramics be adapted to glass cast in a full-sized canister of heat-generating waste, or will smaller individual pieces of glass have to be converted to the glass-ceramic form and then repackaged in canisters?

- What are the long-term radiation effects in such a multiphase system, both with respect to alpha decay and transmutation localized in crystals?

Phosphate Waste Glasses

Phosphate glasses have found little industrial application; therefore the large body of commercial experience and well-developed technology that exists for the various silica-based glasses do not exist for the phosphate glasses. Nevertheless, phosphate glasses have been quite widely investigated for use in radioactive waste immobilization. This is because:

- low-melting glasses are formed readily
- all-liquid processing is possible, reducing the dusting problem sometimes associated with silicate glass manufacture
- the solubility of some waste constituents is higher in phosphate glasses than it is in silicate glasses.

The major development of phosphate waste glasses started at Brookhaven National Laboratory (Tuthill, 1967) and culminated in the manufacture of 11 canisters of radioactive phosphate waste glass during the Waste Solidification Engineering Prototypes (WSEP) program at PNL (McElroy, 1970; McElroy, 1971). The WSEP program showed that phosphate glass had several shortcomings when compared with silicate glasses. The shortcomings included: 1) high ruthenium volatility during denitration of the liquid waste slurry, 2) extreme corrosivity of the phosphate melt, which required use of platinum melters and placed limitations on the melt temperature in metal canisters, 3) rapid thermal devitrification at temperatures above 500°C, and 4) a factor of 1000 increase in the leach rate of the glass after devitrification. Russian development is emphasizing aluminophosphate glass formulations which decrease this problem (Brezhneva, 1976).

The ease with which low-melting phosphate glass formulations can be made continues to intrigue investigators. In the PAMELA process (Heimerl, 1975), initially developed by the Gelsenberg Company in Germany, and now being developed as a co-venture with Eurochemic at Mol, Belgium, the phosphate glass is formed as small beads, which are then placed in a metal matrix in a steel canister. The small bead shapes, plus the high thermal conductivity of the metal matrix, assure that the phosphate glass does not devitrify.

2.2 EFFECTS OF PROCESSING CONDITIONS

Even though chemical composition is the factor most controlling glass properties, the properties will also be affected significantly by processing parameters. Therefore, any consideration of glass properties must include information on how the glass was made or processed. Significant process parameters include:

- degree of mixing of constituents prior to melting
- processing temperature
- degree of melt agitation
- time at processing temperature
- materials of construction for melt containment
- rate of cooling from processing temperature to storage temperature.

Radioactive waste glass processing must be done remotely; therefore, it is important that the process be simple and reliable.

2.2.1 Elements of Typical Waste Glass Processes

The steps common to most waste glass processes are shown in Figure 5. The process must bring the HLLW and glass-making additives together with heat to form molten glass. The molten glass can be made either in the canister in which it is to be stored (batch melting) or it can be made in a continuously-operating melter that discharges melt to the storage canister (continuous melting). Primary examples of batch melting processes are the in-can melting process (Blair, 1976) and the HARVEST process (Warner, 1976). Examples of continuous melting processes include the AVM (Jouan, 1976), the joule-heated melter (Chapman, 1978), and the PAMELA process (Heimerl, 1975). Many other waste glass processes have been described but they all represent variants of batch or continuous melting (ERDA, 1976).

2.2.2 Feed Preparation (Premixing and Calcination)

Many different methods of feed preparation are used in waste glass processing. The methods range from: 1) mixing the glass additives with the HLLW and feeding the liquid slurry directly to the melter, to 2) converting the HLLW to an oxide powder in a separate calciner after which it is combined with dry glass-making

A. BATCH MELTING

B. CONTINUOUS MELTING

FIGURE 5. Alternative Modes of Waste Vitrification Processing

additives and fed to the melter as a dry mixture. All evidence indicates that the method used for feed preparation is without effect on waste glass properties. Adequate mixing of waste and glass-making additives can be achieved by liquid or solid feed preparation, or combinations of the two.

2.2.3 Melting

Melting is the crucial processing step. Several factors must be considered in selecting the melting conditions to use in waste glass processing.

Processing Temperature and Melter Residence Time

The liquidus temperature is defined as the maximum temperature at which equilibrium exists between the molten glass and its primary crystalline phase, i.e., at temperatures above the liquidus temperature the primary crystalline phase is completely soluble in the melt. Waste glasses are usually raised to a temperature of 100°C or more above the liquidus temperature. In a composition as complex as that of waste glasses there may be minor crystalline phases whose liquidus temperature is not exceeded at the operating temperature. Examples of crystalline phases that may exist in minor concentrations (total less than 5 vol%) at the melting temperature are RuO₂, or ruthenium metal, palladium metal, spinel and CeO₂. These are all inert crystalline phases and do not effect the quality of the solidified waste glass. Raising the operating temperature as much as 300 to 400°C does not dissolve any of these phases except CeO₂, which is usually completely dissolved in waste glasses melted above 1200°C.

Waste vitrification processes emphasize low melting temperatures to increase operating reliability. By melting in the range of 950 to 1150°C, corrosion is reduced and volatilization from the molten glass is decreased.

Waste glasses, because of their relatively low ratio of network formers to intermediates and modifiers, have relatively low viscosities (5 to 200 poise) at the operating temperature. The low viscosity assists in establishing equilibrium conditions quickly. Experience has shown that a residence time of 2 to 4 hr at the operating temperature is sufficient to produce good quality waste glass.

Agitation of the melt has been experimented to increase the capacity of low residence time melters (Bonner, 1974). Conceptually melt agitation could increase the homogeneity of the product glass, but because of increased operating complexity, it is not included in any well-developed waste vitrification process.

Volatility During Melting

Although volatility is minimized by the low melting temperatures used in waste vitrification, some waste constituents do have a significant vapor pressure in the melter. This means that some constituents of HLLW will not be incorporated in the waste glass but will go with the off gas. In particular, volatiles which could later cause pressurization of the canisters containing the product glass are removed. The product glass contains less than 0.001 wt% nitrate and 0.2 wt% H₂O.

Another significant constituent that is volatilized is the long-lived fission product ¹²⁹I. It is estimated that about 0.5% of the ¹²⁹I in spent fuel will be in the HLLW. It will all be volatilized during vitrification. The volatilized ¹²⁹I will be scrubbed from the off gas and disposed of separately. Most chloride present in the HLLW will also volatilize during vitrification. Fluoride exhibits a lower volatility and can be incorporated in waste glass; a small fraction may volatilize but it can be recycled.

Radioactive waste constituents which are partially volatile can also be recycled back to the glass process to achieve almost total incorporation in the glass. Recycling is usually done by returning an off-gas condensate stream to the HLLW. HLLW constituents having radioactive isotopes and which exhibit a minor volatility that will be recycled include cesium, ruthenium, technetium, antimony, and tellurium. Solid adsorbents have also been used to collect volatile ruthenium, which can be recycled directly to the melter (Elliot, 1963).

In summary, the minor fraction of the radioisotopes in the HLLW that are volatilized during vitrification are recycled so that they all are incorporated in waste glass. The exception is ¹²⁹I, which is not retained in waste glass.

Corrosion During Melting

Waste glass is melted either in refractory ceramic melters or in metallic

melts. The refractory ceramic melters are designed for a lifetime of several years. The corrosion rates are <0.001 mm/hr. The corrosion product concentration is too low to have any effect on waste glass properties.

The corrosion rate of metallic melters, other than platinum melters, may, however, result in minor and apparently inconsequential effects in the solidified glass. Continuous metallic melters are designed to have lifetimes of 3 to 6 mo, and typically are made of high nickel alloys such as Inconel® 601 or Inconel 690. The corrosion product concentration in the melt is inconsequential because of the very low corrosion rate of the special alloys. Batch metallic melters, however, such as used in the in-can melting process and the HARVEST process, are typically made of stainless steel. Spalling of oxide from the stainless steel surfaces above the melt has been observed. The spall collects as inclusions in the glass towards the bottom of the melter, but does not affect the durability of the glass (Mendel, 1977). Canister corrosion rates beneath the melt surface are <0.01 mm/hr.

Corrosion creates a reducing potential at the stainless steel/melt interface, which on a microscale has been observed to change glass properties. For instance, CeO_2 , which is partially insoluble at the melting temperature, is not observed near the stainless steel surface because the cerium is reduced to Ce^{+3} which is more soluble in the glass (Turcotte, 1978).

Oxidation-Reduction During Melting

The example cited above is one effect that changing the oxygen potential in waste glass can have. Normally waste glass is in a highly oxidized state because of the nitrate in HLLW. In some situations it may be desirable to reduce the oxidation potential in waste glass. For instance, at high fission product loading, liquid-liquid phase separation of a mixed alkali-alkaline earth molybdate salt can occur in borosilicate waste glasses. Reducing the molybdenum to a tetravalent or lower state, or to the metal, prevents phase separation of the water-soluble molybdate salt. It has been demonstrated that silicon metal added to the melt batch can effect the desired reduction of molybdenum (Ross, Patent, 1978). Some other constituents of the

waste glass melt may also be reduced to the metal when silicon is added. The reduced metal then appears as globules, usually less than 2 mm in diameter, suspended in the solidified glass. The metal globules are alloys, often rich in tellurium, which do not affect the overall properties of the waste glass (Ross, 1978).

2.3 CANISTERIZATION AND POST-FILL EFFECTS

After the waste glass is fused to the desired molten state, it is confined in a steel canister for cooling and subsequent handling and storage. From this point on the waste glass and its canister should be considered as a unit.

2.3.1 Canister Design

The canisters are designed to package the waste in convenient increments for handling during storage, transportation, and emplacement in geologic disposal. In most safety analyses, credit is taken for the canister's barrier potential during surface storage and transportation; no credit is taken once the waste is in the geologic repository.

The development of cracks or other minute leaks, in a small fraction of the canisters cannot be totally guaranteed against, thus the concepts of overpacking and additional engineered containment are being evaluated. Overpacking refers to recanning the waste canister in a secondary canister slightly larger than the first. Overpacks can provide redundant protection while the waste is on the surface. Engineered containment refers to man-made barriers provided to protect waste capsules during geologic storage, and can take many forms, such as combinations of metal overpacks, thick-walled ceramic or graphite receptacles, or special back-fill of adsorbent or water repellent materials. Engineered containment can be devised that will assure integrity of the waste capsules for a certain limited time in geologic repositories. Such integrity cannot be assured for very long times, but can be designed to serve for potentially useful periods, i.e., to allow relatively easy retrieval for a predetermined period (perhaps 50 yr), or to permit decay of ^{90}Sr , the isotope initially present in the most hazardous concentrations (perhaps 500 yr). Discussion of additional engineered containment is outside the scope of this

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report, which is limited to waste glass and the canister it is initially placed in.

As outlined in Figure 5, canisterization of waste glass can be carried out in two ways. In batch melting, the glass is formed directly in the canister. In continuous melting the molten glass is withdrawn from the melter and transferred to the canister. This can be a direct transfer, or the glass may be formed into beads or marbles before being placed in the canister. In all cases the major elements of canister design and configuration are the same. Waste glass canisters are usually fabricated from standard stainless steel pipe and have the shape of a right cylinder. Mild steel can be used if melting does not take place in the canister.

Canister Size

Limitations on canister size are due to handling and heat removal considerations.(a) In particular, handling considerations limit canister weight and length, and heat removal considerations limit diameter. The weight may be limited to about 4 tons (Moore, 1978). Diameters which have been considered range from 5 to 48 in., but most attention has been focused on the 8- to 24-in. range. Waste canister lengths can also vary widely. In Europe plans generally call for 3- to 6-ft long canisters. In the U.S. attention has focused on 10- to 15-ft lengths.

The amount of self heating in high-level waste depends on the radioisotope content in the waste, which is a function of fuel irradiation, time out-of-reactor, and the reprocessing flowsheet used. Vitrification of short-cooled power reactor waste (times as short as 180 days out-of-reactor have been considered) with a low inert content can yield waste glass with a self-heating power level of over 300 W/l. Such a borosilicate waste glass was made

in the Waste Solidification Engineering Prototypes (WSEP) program in a 6-in. dia canister (McElroy, 1972). More likely initial power levels in waste glass are 10 to 100 W/l for power reactor waste and 0.01 to 1 W/l for defense waste. The higher waste heat loadings are accommodated by varying the diameter of the waste canister. Smaller diameter canisters are used to accommodate higher heat loadings. The principal factors to be considered are maximum allowable centerline temperature and maximum allowable surface temperature. The maximum allowable surface temperature is set to minimize sensitization of the stainless steel and because of in-cell handling considerations; it is about 375°C. The maximum allowable centerline temperature for waste glass is determined by 1) devitrification, or 2) gravity settling. The effects of devitrification of waste glasses are described in Section 3.3.2. In view of the relatively minor effects of devitrification found in tests to date, restricting the centerline temperature for this reason appears unnecessary.(b) If no limit is placed on the amount of devitrification then the next limiting centerline temperature is about 900°C. At this temperature, glass at the canister centerline will be partially melted. If this state is maintained for many days, an undesirable settling of crystalline species, such as ruthenium, could occur.

For a given waste heat loading and canister size, waste glass thermal conductivity determines the centerline temperature. Waste glass thermal conductivity is relatively independent of glass composition (see Section 3.2.4). The use of internal metal fins approximately doubles the effective thermal conductivity of the contained waste glass (Blair, 1976). Metal matrices can increase the effective thermal conductivity by a factor of 10 to

- (a) In addition to heat removal considerations during handling and interim storage, total heat output becomes a factor when the canisters are transferred to a geologic repository. Geologic repositories will place a limit on the maximum heat generation rate per canister (kW/canister), and perhaps on the heat generation rate per unit length of canister (kW/ft). The duration of the interim storage period determines whether the initial heat removal considerations or the later repository requirements are limiting. Analyses have shown that unless the interim storage period is considerably longer than 10 yr, the repository requirements will limit the size (or waste loading) of canisters containing power reactor waste glass (McElroy, 1972).
- (b) Phosphate glass is an exception, particularly formulations which contain significant concentrations of sodium. High-sodium phosphate glasses devitrify rapidly. They are porous and have a thousandfold higher leach rate when devitrified. The high thermal conductivity of the lead matrix used in the PAMELA process canisters maintains the centerline temperature well below 450°C (VanGeel, 1976).

30 but the volumetric waste loading is reduced by about 30% (Jardine, 1978).

Obviously many parameters are involved in canister sizing. The parameters are well understood and may be reviewed in detail (McElroy, 1972; Hoskins, 1976; Jardine, 1978). For general purposes, it may be assumed that in the U.S., power reactor waste glass canisters will be 1 ft in dia by 10 ft long and defense waste glass canisters will be 2 ft in dia by 10 ft long.

Materials of Construction

Materials of canister construction are selected on the basis of corrosion resistance (both at the internal glass/canister interface and the external environment/canister interface), high temperature properties, ease of decontamination, and economics. Stainless steel, in particular 304L stainless steel, has been used with good success in most of the U.S. development studies. Many other high nickel-chromium alloys have also been investigated as materials for waste glass canisters (Slate, 1978). Carbon steel canisters can possibly be used with continuous melting processes; their use was demonstrated with radioactive glass in the WSEP program (McElroy, 1972).

In general, waste glass canisters are made from standard pipe, usually Schedule 10 or 20 for low-temperature filling (page 19) and Schedule 40 for high-temperature filling (page 20).

Compatibility with Overpacking

Design of the primary canister should minimize protuberances to facilitate overpacking. If the overpack is close-fitting an airfilled annulus may provide satisfactory heat transfer. Alternatively, the annulus may be filled with a heat transfer medium.

Overpacking may be done routinely, or only nonroutinely when required by off-standard conditions in the primary canister. Reasons which have been forwarded for routine overpacking include: 1) to provide a stress-free outer canister (this requires stress relief of the seal weld area), 2) to assure low surface contamination of the outer canister, or 3) to provide redundant protection, e.g., the overpack canister could be of a different material, selected to counterbalance weaknesses (to chloride attack, for instance) in the protection afforded by the primary

canister. However, a recent study concluded, "... the use of an overpack, as an integral part of design results in an undesirable design and economic constraint on the waste management system" (Birmingham, 1978).

Presently, there is not a consistent approach to overpacking. The only industrial waste vitrification plant now operating, the French AVM, does not overpack its canisters; however, preliminary design of the Savannah River Project defense waste calls for overpacking all canisters. For the purposes of this report it will be assumed that only canisters that do not pass post-fill inspection, or which develop leaks during interim storage, will be overpacked. Most of the canisters will not be overpacked.

2.3.2 Canister Filling

Many methods of filling canisters with waste glass are being considered. The methods can be divided into two categories, high-temperature and low-temperature filling, which roughly correspond to batch melting and continuous melting, respectively (Figure 5). The dividing line is about 700°C. In general, low-temperature filling decreases the potential for canister corrosion and devitrification of the contained glass. Carbon steel canisters can be considered when low-temperature filling is utilized; stainless steel canisters, or their equivalent, must be used with high-temperature filling.

Low-Temperature Filling

Low-temperature filling requires that the glass be formed in a separate vessel and transferred to the canister. Canisters can be filled either with molten glass or with solidified glass, e.g., glass marbles. The most important factors are the absolute temperatures and the rate of change in temperature to which the glass is exposed.

When canisters are filled with molten glass, the main concern is that the glass flows to fill the canister and does not leave void spaces. This requires a residence time of a few minutes above 700°C. This temperature can be maintained when molten glass is rapidly dumped into a canister with wall temperature initially at room temperature. The latent heat is sufficient to permit uniform filling. Rapid dumping into a cooled canister produces many hairline fractures in the

solidified glass. If the flow of molten glass into the canister is slow, coinciding with the processing rate in a continuous melter, for instance, then the canister wall temperature has to be held at about 600°C to obtain uniform filling of the canister.

If the waste glass is formed into marbles before being placed in the canister, as in the PAMELA process, then the glass is rapidly cooled without being fractured during the marble-forming step. Ideally, the glass will be reheated to the temperature of the molten metal (about 350°C for the currently preferred lead or lead-based alloys) before the molten metal fills the interstices around the glass pieces.

High-Temperature Filling

High-temperature filling is usually utilized only when the glass is formed in the canister, as in batch-melting (Figure 5). In the batch processes the temperature must be held for a minimum of 2 to 4 hr at the processing temperature (always 950°C or higher). Zone-heated furnaces can be used so that the entire canister does not have to be held at the processing temperature during the entire fill cycle, which is usually 12 to 24 hr. When the glass in a given zone is thoroughly melted, that furnace zone is turned off. Thus, even in high-temperature filling the time any one segment of the canister need be at processing temperature is not more than a few hours.

2.3.3 Canister Cooling

Several factors must be considered in determining the cooling regime for the waste-glass-filled canisters. Options range from water or air quenching to slow annealing in controlled-temperature furnaces or kilns. Most current process designs use a compromise approach of controlled cooling and air quenching, which maintains the cooling rate in the range of 50 to 100°C/hr. Thermal stresses set up by this cooling rate result in some fracturing of the glass. Fracturing is greatest near the canister wall because self-heating reduces the cooling rates in the interior of the canister. Studies have shown that the fracturing increases the surface area of the glass in the canisters about a factor of 10 to 15 over the surface area if the glass block remained as a monolith.

Stress in the Canister Walls

During cooling, the walls of the canister become stressed due to the fact that glass shrinks less as it cools than does steel. The stress is induced only in the temperature range below the glass transition temperature ($525 \pm 25^\circ\text{C}$ for most waste glasses). Above the glass transition temperature the glass is plastic and readily accommodates changes in canister dimensions.

Stresses in the walls of canisters of cooled waste glass have been calculated to be about 35,000 psi, enough to cause slight plastic deformation of the canister. The stresses have been confirmed experimentally in 304L canisters containing nonradioactive simulated borosilicate waste glass (Slate, 1978).

The fact that the canisters are stressed may make them more susceptible to chloride-induced stress-corrosion cracking during water basin storage (Mecham, 1976). Water quality in the basins is carefully controlled, thus, chloride impurities in the basin water should always be below the threshold that can accelerate stress corrosion cracking. Stress-corrosion cracking is also minimized when the pH of the water is maintained at pH 9 or above (Scherfstein, 1958).

Stress in the canisters is actually beneficial to waste glass quality since it places the glass in compression. Glass is strongest under compressive forces. The compressive forces also tend to hold the surface of any cracks which may exist in the glass body in tight contact with one another.

Since stress is induced in the canisters only at temperatures below 525°C it occurs in about equal severity in high-temperature and low-temperature filled canisters. If required, several techniques can be considered to minimize tensile stress in the canister wall. The techniques, which require further development, include collapsible canister liners, rapid quenching, and ballpeening the exterior.

Sensitization of the Canister Walls

Sensitization refers to a temperature-sensitive phenomenon that can occur in high-chromium ferrous alloys, such as 304L stainless steel. At temperatures between

500 and 750°C chromium carbides tend to precipitate at the grain boundaries, after which the metal is more susceptible to intergranular corrosion. Sensitization is a reversible time-temperature dependent phenomenon, as shown in Figure 6. Near the extremes of the sensitization temperature range many months may be required before significant sensitization occurs. At the temperature where the sensitization rate is maximum, measurable sensitization may occur in 30 min and undesirable sensitization may occur within 6 hr. Therefore, the canister wall cooldown rate is generally maintained at 50°C/hr or higher in the range of 500 to 850°C. Desensitization of sensitized surfaces occurs at temperatures above 850°C. Several alloys are available which are much less susceptible to sensitization than 304L stainless steel. Among these are various Inconels and Hastalloys.

FIGURE 6. Time-Temperature Sensitization Behavior of 304 Stainless Steel, Effect of Carbon Content (Solomon, 1978)

Devitrification

Slow cooling through the temperature range of 950 to 500°C can result in some devitrification of waste glass. If the cooling rate is 50°C/hr or more the devitrification occurring during canister cooldown is negligible. Devitrification of waste glass is discussed in much greater detail in Section 3.3.2.

Thermal Stress Fracturing

Waste glasses have thermal expansion coefficients in the range of 70 to 90×10^{-7} in./in.-°C, similar to commercial bottle glasses. This means that rapid temperature changes can induce thermal stresses in waste glasses sufficient to cause them to fracture. Calculations indicate that the thermal stresses in an 8- to 16-in. dia canister of waste glass cooling at 100°C/hr can be relieved when cracks form at approximately 2-in. intervals. This corresponds roughly to the amount of fracturing which is actually observed in nonradioactive glass canisters cooled at 100°C/hr. Faster cooling causes more fracturing near the canister wall/waste glass interface.

2.4 POST-FILL OPERATIONS

Post-fill operations are the operations which are carried out after the canister is filled and before it is placed in interim storage. Post-fill operations include seal welding, quality assurance, and decontamination.

2.4.1 Seal Welding

The opening through which waste is loaded into the canister is sealed by welding a cap over the hole. The use of welding to close the opening assures that the sealed canister has uniform overall integrity and that the canister will be a reliable outer barrier in the waste glass-canister package.

Many different canister closure designs have been tested which could be used in routine remote operation. Several remote units have been designed and tested. The welding techniques utilized include tungsten inert gas (TIG), inertia and resistance upset (Slate, TBP). During the WSEP program, TIG welding was used (McElroy, 1972).

2.4.2 Quality Assurance

Quality assurance, or product quality verification, refers to the operations which are carried out to show that the filled canisters of waste glass have the required properties. As stated earlier, precise definition of the required properties is still evolving; nevertheless, it is possible to discuss the necessary product quality assurance in general terms.

The quality assurance applied to the waste canister differs in important ways

from that applied to the waste glass. Quality assurance techniques applied to the canister are the standard procedures that have evolved over many years for the fabrication of metal vessels or containers. Hands-on inspection of each canister prior to filling, with the rejection of off-standard canisters, is possible.

In contrast to the canisters, waste glass is a more recently developed, highly radioactive substance for which quality assurance techniques are still evolving. Hands-on inspection is, of course, impossible and, once the glass is in the canister, the types of remote measurements which can be made to corroborate quality are somewhat limited. Therefore, process control becomes an important part of waste glass quality assurance.

Process Control

By properly controlling the waste glass process, it is possible to produce waste glass within certain specifications. Process control parameters of particular importance are listed below:

- Analysis of the liquid waste being fed to the vitrification facility: Both chemical and radioisotopic content of the incoming waste must be known. The former affects the composition of the product glass; the latter determines self-heating and radiation effects in the glass and the radiation dose rate from the canisters.
- Glass additive composition: Glass-making additives can be added to the waste in a feed tank prior to processing, or they can be metered into the process continually. Both methods have proven satisfactory.
- Input stream flow ratios: Only two streams are involved, the liquid waste and the glass additives. They must be mixed in a predetermined ratio to form the desired glass. Tests have shown that while it is possible to control the ratio closely, fluctuations of 20% on the high side for the waste and 20% on the low side for the glass additives are permissible without changing waste glass properties significantly. Fluctuations on the low side for the waste and on the high side for the glass additives are usually even less significant; the main effect is the production of a more dilute waste loading in the glass.
- Processing temperature: Waste glasses are formulated to be melted at a certain temperature for a certain length of time somewhere between 950 and 1150°C, usually at least 2 hr. If these nominal conditions are not met the product may contain waste oxides which are incompletely dissolved in the glassy matrix.
- Topping off of filled canisters: Canisters are usually 80 to 90% filled with glass. In the processes in which waste glass is formed in the canister, precautions should be taken that no residue of unmelted waste calcine remains on top of the last glass melted in the canister. These precautions could involve the addition of some glass additives without waste, followed by holding the top of the canister at the processing temperature for an additional 2 to 3 hr.
- Cooldown of canisters: The temperature regime used for cooling down canisters of waste glass is designed to minimize sensitization of the canister walls and devitrification of the glass. This means a rapid cooldown (>50°C/hr) to a temperature of approximately 500°C.

Standard reliable techniques can be used for most of the waste glass process control requirements listed above.

Measurements on Product Glass and Filled Canisters

As described in the previous section, process control can be used to regulate waste glass compositions and verify the quality of the final glass/canister package. The efficiency of process control, however, will be corroborated by certain measurements, made either routinely or as spot checks, on the product. These checks will include some, or perhaps all, of the following measurements:

- Analysis of waste glass: Quality assurance usually includes analyses of the product to determine if certain desired properties are within specifications. As described earlier, specifications have not been established for waste glass. The most probable analysis that would be performed on waste glass samples is a leach test. The leach rate of the glass would probably be determined after a prescribed thermal treatment designed to produce the maximum temperature effects anticipated in the waste glass. Several sampling techniques are

available, ranging from taking an aliquot of waste calcine and melting it with the requisite amount of glass additive in the hot laboratory, to taking "grab" samples of the molten glass pouring from a continuous melter. The WSEP program demonstrated that it is even possible to core-drill samples from a filled canister and reseal the hole in the canister wall. Processes, such as the PAMELA process, in which glass marbles or other free-standing shapes are produced, facilitate sampling of the product. Analyses made on waste glass samples will probably be too time consuming to be used as a control on each canister. More likely a sample(s) will be used to certify the quality of all of the canisters in a given run period made from a batch of similar waste solution.

- Physical inspection: Each canister will be weighed and checked for dimensional stability during processing, i.e., changes in diameter, roundness, or longitudinal warpage which could conceivably result from filling the canister with glass. The bulk density of the product glass will be calculated from weight and volume. In addition, each canister will be checked visually for obvious defects.
- Radiation field: Measurements of the magnitude and uniformity of the gamma and neutron fields associated with waste glass canisters will help to: 1) corroborate the radiochemical analysis of the liquid waste fed to the process, 2) define transportation shielding requirements, and 3) determine the homogeneity of the waste glass.
- Heat generation: Measurement of the heat-generation rate of waste canisters will also help to corroborate the radiochemical analysis of the liquid waste fed to the process. Knowledge of the heat generation rate of each waste glass canister is required at the geologic repository since there will be a maximum integrated heat-load limitation at each repository. Various types of calorimeters can be used to measure the heat generation rate of individual canisters. Alternatively, the heat-generation rate can be calculated if the surface temperature of the canister and the emissivity of the canister surface is known (McElroy, 1972).
- Weld quality: The leak tightness of the seal weld can be checked with a helium mass spectrometer leak tester, using the

technique applied in the WSEP program or by modifications of that technique (Kelly, 1968; McElroy, 1972). The quality of the weld joint can be checked by dye penetrant or ultrasonic testing. X-ray examination is not practical in most cases because of the high-radiation field in the waste solidification cell.

- Nondestructive testing: The nondestructive testing technique which has been most applied to waste glass canisters is ultrasonic scanning, particularly to check for gross corrosion of the canister wall. It has been suggested that ultrasonic techniques may have application in measuring the amount of fracturing in canisterized waste glass, but no successful tests have been made.

Canisters which are identified as off-standard by the afterfill quality assurance procedures will be overpacked before they leave the processing cell.

2.4.3 Decontamination

The final step before the waste glass canisters leave the processing cell is decontamination of the external surfaces. This is done to minimize introduction of contamination into the interim storage facility, which is usually a water basin but which could be an air-cooled dry storage facility such as the one at the AVM vitrification facility at Marcoule, France. The interim storage facilities are equipped with filters, ion exchange beds, etc., to handle minor releases of radioactivity; therefore, stringent decontamination of the canisters is not required. The main goal is removal of loosely adhering particles, i.e., the smearable activity.

Tests made with the WSEP canisters have shown that high-pressure water jets are quite effective in removing smearable activity. A similar decontamination procedure is being used for the AVM canisters. Another more vigorous procedure using electropolishing is being developed and could be applied to the decontamination of waste glass canisters (Allen, 1978). It has also been demonstrated that canisters will self-clean while being stored in water basins.

Decontamination, which uses solutions at 100°C or less, will subject high heat-load waste-glass canisters to temperature changes. A further temperature change occurs when the canisters are placed in interim storage. This change is due either to a further decrease in temperature to 50

to 60°C, if the storage is in water, or due to a probable increase in temperature if the canisters are placed in air storage. As described earlier, thermal stress during initial cooldown will produce some

fractures in canisters of waste glass. Subsequent thermal cycling, such as that occurring in decontamination and emplacement in interim storage, should not add significantly to the fractures already present.

1 INTRODUCTION

2 FORMATION OF RADIOACTIVE WASTE GLASS

3 PROPERTIES OF RADIOACTIVE WASTE GLASS IN CANISTERS

CONTINUED TESTING IS YIELDING A GOOD UNDERSTANDING OF PROPERTIES AFFECTING THE LONG-TERM STABILITY OF CANISTERIZED WASTE GLASS

4 STABILITY OF CANISTERIZED RADIOACTIVE WASTE GLASS DURING HANDLING, STORAGE AND FINAL ISOLATION

FIGURE 7. Waste Glass Specimens Doped with 8 wt% $^{244}\text{Cm}_2\text{O}_3$ After Cumulative Radiation Dose Corresponding to 500,000 Years Storage

a. CORE-DRILLING TO OBTAIN WASTE GLASS SAMPLES FOR CHARACTERIZATION FROM CANISTERS PRODUCED IN NONRADIOACTIVE PILOT PLANT

b. VIEW THROUGH LEAD GLASS WINDOW OF 8-YEAR OLD CANSITER OF BOROSILICATE WASTE GLASS WHICH CONTAINED 1,400,000 Ci WHEN PREPARED. (NOTE PLUGGED CORE-DRILL HOLES FROM WHICH SAMPLES OF RADIOACTIVE GLASS WERE REMOVED FOR CHARACTERIZATION.)

FIGURE 8. Waste Glass Canisters Prepared in Nonradioactive and Radioactive Pilot Plants at PNL

3.0 PROPERTIES OF RADIOACTIVE WASTE IN CANISTERS

Section 2.0 of this report provided background on how canisterized glass is prepared. The properties of canisterized glass will now be examined in detail. The probable behavior of the canisters and the glass in the subsequent situations to which they may be exposed will then be discussed in Section 4.0.

Basically, canisters are well understood. Stainless steel has been in use 50 yr and its behavior in various types of service is well documented. Some of the nickel-base alloys, also being considered as canister materials, may be more recently developed but they were designed for severe service and have been well tested. Waste glass, on the other hand, although it resembles commercial glass and enamels, is essentially a new material. Therefore, a greater emphasis has been placed on a detailed characterization of waste glass properties. Detailed characterization has been done on laboratory prepared specimens, including specimens with high-induced radiation doses, as shown in Figure 7. Many tests have been performed on waste glass prepared in engineering-scale equipment, both nonradioactive and radioactive, as shown in Figures 8a and 8b, respectively, which corroborate the laboratory-scale results.

3.1 CANISTER PROPERTIES

Canisters are designed to contain waste glass in convenient packages for handling and shipping, and to act as a primary protective barrier until the waste is put in a geologic repository. Corrosion experts believe there is no way to guarantee against the possibility that a very small number of canisters may develop pinhole leaks or hairline cracks in water basin storage. These canisters can be overpacked.

To predict their long-term behavior, it is important to understand the changes in the properties of the canisters, if any, which occur as a result of operations

within the processing cell and in subsequent operations. The canister operations include filling with glass, closure welding, after-fill quality assurance, and decontamination within the processing cell, plus interim storage and transportation outside the cell. Many nonradioactive engineering-scale runs, plus about 200 radioactive engineering-scale runs in the U.S., France, and England have demonstrated that the changes in the canisters are minor and, if proper precautions are taken, do not affect their integrity.

The present canister material of choice is 304L stainless steel. Other materials of construction are being considered in development programs, but most of the canister experience in the U.S. is with 304L SS. All tests indicate that it is a satisfactory canister material for either high- or low-temperature canister filling. Most foreign experience is also with canisters of various kinds of stainless steel.

A basic premise in the conclusion that the canisters will maintain their integrity is that, once processing is completed, a limit will be maintained on the maximum permissible canister wall temperature. The maximum permissible wall temperature set during the WSEP program was 425°C. It is probable that this will be lowered, perhaps to 375°C, for routine operations in a processing plant. The limit prevents sensitization of the canister metal and greatly lowers the potential for corrosion.

3.1.1 Physical Distortion

The stress in the canister wall due to the mismatch between thermal expansion coefficients of waste glass and stainless steel has already been described (p. 18). This does not affect the strength of the canister; it may somewhat increase the potential for corrosion. No warping or bowing of waste glass canisters has been observed, even canisters as large as 36 in. in dia and 10 ft long.

3.1.2 External Corrosion

The potential for external corrosion is greatest during processing and water basin storage. Air oxidation during processing can result in some oxide scale formation, as discussed in Section 2.2.3, but if the process is operated within design limits, the depth of overall penetration is less than 2 to 3 mil.

A few isolated canister leaks during water basin storage must probably be expected. With proper control of conditions, the frequency of leaks can be kept very low. The frequency is estimated to be less than one per thousand canisters. (a) Any leaks that occur will probably be due to intergranular attack producing a short hairline crack that would expose only a small area of waste glass to the basin water. Remedial action would be removal of the canister to a hot cell where it would be thoroughly dried out and overpacked.

Factors that contribute to reducing corrosion potential during water basin storage include:

- water quality control, including control of Cl^- and pH
- minimizing sensitization of the canister wall during the glass-filling operation and during closure welding
- removing as much surface scale as possible during the decontamination step, thus reducing crevices that could become sites for crevice corrosion.

No mechanisms have been identified which could cause canister leaking during interim air storage.

3.1.3 Internal Corrosion

The corrosion rates during canister filling are well known. Processing conditions are selected to maintain the overall corrosion below 15 mils (less than 5% of the wall thickness). Once the canister is removed from the process the potential for internal corrosion from borosilicate waste glass is almost nonexistent. Examination of the radioactive WSEP canisters after

various times of storage has shown little internal corrosion at the waste glass-canister interface. Similarly, nonradioactive laboratory experiments at storage temperatures ($<375^\circ\text{C}$) have also shown negligible corrosion at the glass-canister interface (Slate, 1978).

3.1.4 Radiation Effects

Aside from the high temperatures during processing, the only other unusual conditions to which the canisters are exposed is the high radiation field of the waste glass. Stainless steel serves reliably in nuclear reactors and nuclear processing vessels where radiation fields exceed those of waste canisters. It may be concluded that radiation will not adversely affect waste glass canisters.

3.1.5 Pressurization Behavior

As stated earlier, one of the advantages of glass as a waste form is that volatiles will not be released from the solid waste during temperature excursions or by radiolysis. The only mechanism that has been identified which could create any appreciable pressure in a canister of waste glass is helium buildup from alpha decay and this is limited to wastes of very high actinide content (see Section 3.5.6). The effects are minimized by assuring that the canisters are not more than 90% filled with glass, leaving sufficient vapor space to accommodate the released helium without excessive pressure formation.

Waste canisters are not designed as pressure vessels. This is a further safety feature. In the event of excessive internal pressurization, venting would occur before explosive forces could build up in the canister.

3.2 PHYSICAL AND MECHANICAL PROPERTIES OF WASTE GLASS

The physical and mechanical properties of radioactive waste glass are innate properties which may be treated generically. They are relatively independent of composition and are of much the same magnitude for most waste glasses.

- (a) One WSEP canister leaked in storage. However, its storage history was nontypical and stress corrosion cracking would have been predicted. The 310 stainless steel canister from Run SS-9 was thoroughly sensitized by storage in air at 400°C for 3.5 yr, and was then stored in water containing Cl^- . The canister began leaking after about 10 mo in water (Bradley, 1977).

3.2.1 Viscosity and Softening Point

Waste glasses are formulated to have a viscosity of 5 to 200 poises at the processing (melting) temperature, which is usually within the range of 950 to 1150°C. The viscosity of waste glasses is contrasted with that of commercial glasses in Figure 9.

FIGURE 9. Viscosity of Typical Waste Glass

Some important properties of waste glass can be related to viscosity. The softening temperature (Littleton softening temperature) of glasses is defined as the temperature at which the viscosity is $10^{7.6}$ poises. This is the temperature above which the glass cannot support its own weight and begins to slump. Cracks in the glass will heal rapidly at the softening temperature, which is about 575 to 650°C for most waste glasses. The glass transition temperature is the temperature at which the viscosity is about 10^{13} poises. For waste glasses this usually is in the range of 500 to 550°C. As described earlier, glass is plastic above the glass transition temperature and thus is not susceptible to fracture.

3.2.2 Density

Density is probably the only physical and mechanical property of waste glass

that will be routinely measured at an operating plant. The bulk density, as determined from the weight and height of the glass column in the canister, can serve as a quality control check.

The density of glass is an additive function of the constituents (Elliot, 1945). Within limits the density of a glass can be predicted from empirically-derived density factors for each constituent. The density factors are related to atomic weight. Thus, waste glasses containing high loadings of fission products, which have higher atomic weights than most usual glass constituents, will be more dense than those with low loadings of fission products. Certain special glass constituents, such as zinc or lead, also markedly increase density.

Common commercial soda-lime-silica glass has a density of about 2.5 g/cc. Depending on waste composition and waste loading, radioactive waste glass densities are usually in the range of 2.5 to 3.3 g/cc. Zinc borosilicate waste glasses may have a density of 3.7 g/cc or higher and the density of a lead borosilicate waste glass may exceed 4.8 g/cc. Radiation over long periods of time can cause changes in waste glass density; maximum change equals approximately 1% (see Section 3.5.3).

For a given glass composition, the density of the final product may vary over 0.1 g/cc depending on the time-temperature curve of its cooling through the transformation range (Figure 4). Thus, bulk density cannot serve as a precise quality control check on glass composition. It can, however, be a convenient quality control check for gross porosity or voids in the canister.

3.2.3 Friability

Friability refers to the fracture behavior of waste glass. Fractures increase the surface area, and the amount of activity released in a leaching situation is proportional to the exposed surface area. Also, the fractures may produce a small fraction of less than $10\mu\text{m}$ dia particles, which are respirable. Friability becomes a factor in safety analyses only when the canister is breached. Canister breaching requires either very high accidental impacts, which are improbable, or; corrosion through the canister wall, which should not occur until well after the waste glass is in a geological repository.

Friability of waste glass is usually measured by impact tests of various kinds, in which either weights are dropped on a glass specimen, or the glass specimen itself is dropped onto an unyielding surface. The most comprehensive impact tests on waste glass yet performed are described by Smith and Ross (Smith, 1975). In these tests, the glass was cast in stainless steel canisters either 2 in. in dia by 4 in. long or 6.6 in. in dia by 52 in. long. The large canisters were dropped onto a concrete pad from heights up to 30 ft (maximum impact velocity equalled 44 ft/sec). The smaller canisters were released in the path of a 75-lb granite block mounted on a rotating arm. Impact velocities up to 117 ft/sec (80 mph) were achieved in this apparatus. None of the large canisters failed in the impact tests; some of the small canisters had small cracks after impacts at 76 and 117 ft/sec, but weight loss measurements showed that no glass escaped through the cracks. After the tests each of the canisters was opened and the particle size of the contained glass was determined. Figure 10 shows the amount of sub $10\text{ }\mu\text{m}$ particles formed as a function of impact velocity. It should be noted that both vitreous and devitrified specimens of the same glass composition were included in these tests and no difference in fracture behavior was observed. Therefore, the curve shown in Figure 10 is based on data from both vitreous and devitrified glass.

FIGURE 10. Effect of Impact Velocity on Fraction of Respirable Particles Formed

Friability is also a function of internal stresses. These are difficult to define but include residual thermally-induced stresses and, over the long term, radiation-induced stresses. As mentioned in the preceding section, radiation can cause slow changes in density. In devitrified glass or crystalline materials, particularly, differing radiation-induced density changes in adjoining phases could lead to localized stresses. The subject of radiation-induced density change is covered in more detail in Section 3.5.3.

Friability is relatively independent of glass composition. Impact tests comparing waste glasses and commercial soda-lime-silica glasses yielded similar results (Bunnell, 1977).

3.2.4 Thermal Conductivity

Thermal conductivity is another physical property of waste glass that is relatively independent of glass composition. The thermal conductivity of most waste glasses falls within the limits shown in Figure 11. The thermal conductivity increases gradually with temperature until the softening point of the glasses is reached. Above the softening point, the increase in the thermal conductivity as a function of temperature is more rapid.

FIGURE 11. Thermal Conductivity of Waste Glasses

The importance of thermal conductivity is that it determines the temperature profile between the glass at the center of the canister and the glass at the canister wall. Higher thermal conductivities give less steep temperature profiles.

3.2.5 Thermal Expansion Coefficient

The thermal expansion coefficient of waste glasses is similar to that of commercial soda-lime-silica glasses. Representative thermal expansion coefficients of waste glass are shown in Table 3. The thermal expansion coefficients are relatively independent of composition. Sodium probably has the greatest effect on thermal expansion of any of the waste constituents. Decreasing sodium content usually decreases the thermal expansion coefficient. (Commercial low expansion glasses, such as Pyrex, have a very low sodium content.)

TABLE 3. Typical Thermal Expansion Coefficients of Waste Glass

Waste Glass Type	Thermal Expansion Coefficient (25-400°C), $\alpha \times 10^{-7}/^\circ\text{C}$
Borosilicate	80-100 (b)
Glass-ceramic	100-120 (c)
Phosphate	90-110 (d)

(a) For comparison, the values for soda-lime-silica bottle glass and Pyrex are 90×10^{-7} and 30×10^{-7} , respectively.

(b) Ross, 1978

(c) De, 1977

(d) Thompson, 1970

A low thermal expansion coefficient gives increased thermal shock resistance and decreases the time required to anneal a block of glass, and thus would appear to be a desirable characteristic. On the other hand, a low thermal expansion coefficient will further increase the mismatch in thermal expansion coefficient between the waste glass and its canister, and thus will increase the stress in the canister wall. The thermal expansion coefficients of waste glass, as shown in Table 3, represent a good compromise between the opposing requirements. In any event, effecting significant changes in the thermal expansion coefficient would probably be very difficult. Sodium, for instance, is almost always present in waste glasses in relatively high concentrations, either because it is an unavoidable constituent of the waste or because it is needed for viscosity control.

3.3 THERMAL EFFECTS AND DEVITRIFICATION

The facilities for waste vitrification and handling of the canisters of waste glass are designed to avoid deleterious temperatures. Thus design limits, based on known glass and canister properties, are placed on the maximum temperatures allowed during waste glass manufacture and storage. For accident analyses, it is necessary to know what will occur when the design temperatures are exceeded.

3.3.1 Volatility

After manufacture, volatility from waste glass is a factor only in accident analyses. Waste glass manufacturing temperatures are several hundred degrees above the maximum design storage temperatures, which assures that any volatiles that might pressurize the canisters during storage have been removed. However, accidents can be postulated, involving external heat sources or clusters of uncooled waste canisters, in which the temperature rises far above normal storage or handling temperatures. Volatility data are available for analysis of these postulated accidents. An example of such data is shown in Figure 12. The data demonstrate that volatility is very temperature dependent. Analysis of postulated accident scenarios is continuing, but accidents in which waste glass could be exposed to temperatures as high as those shown in Figure 12 will be extremely rare.

Volatility experiments with waste glasses show that cesium is the most volatile radioisotope. Although ruthenium often exhibits significant volatility in radioactive processes, its volatility from waste glasses is less than that of cesium.

3.3.2 Devitrification and Phase Separation

Major thermal effects on waste glass are devitrification and phase separation. Both phenomena are very dependent on glass composition, but some effects are common to most compositions.

Devitrification

Devitrification is the formation of crystals caused by the rearrangement of certain atoms in the glassy matrix. Crystals form because their ordered structure has a lower free energy. The ordered structure is more thermodynamically stable than the random network of the glass. The amount and identity of the crystals formed depends on the initial composition of the

FIGURE 12. Volatility of Waste Constl. (Gray, 1976)

glassy matrix. The rate of crystal formation is time and temperature dependent. Measurable devitrification of waste glasses generally occurs only from 950 to 500°C. Above 950°C, the crystals redissolve.^(a) Below 500°C, the viscosity of the glassy matrix is so high that crystallization is diffusion-limited to extremely low rates. The maximum rate of formation of most crystalline species occurs somewhere between 800 and 850°C but the equilibrium yield of crystals is low. At lower temperatures the rate of formation decreases but the equilibrium yield of crystals increases. It is possible to define approximate equilibrium yields at

700°C in experimentally practical times (1 yr). At lower temperatures the experiments cannot be completed in practical times. But the temperature effect above 700°C exhibits Arrhenius behavior and can be extrapolated to lower temperatures. Extrapolation shows that the kinetics are extremely slow at geologic storage temperatures. Below approximately 200°C, measurable crystallization (anhydrous) would require millions of years (Turcotte, 1978). The existence of natural glasses which are millions of years old is an indication that the extrapolation is justified.

It is important to understand what devitrification does to waste glass. Figure 13 shows photomicrographs of a typical waste glass before and after devitrification. It is only on the microscopic scale that the effects are truly apparent. Even totally devitrified waste glass usually includes only 30 to 40 vol% crystals, as compared to 95 vol% in commercial glass-ceramics. To the naked eye the devitrified waste glass is unchanged except that its luster is dulled and the color may change.

Changes in friability due to devitrification are slight, usually within experimental error. Devitrification should not be equated with disintegration. Properly formulated waste glass retains its coherence and strength when devitrified.

Devitrification usually increases the overall leach rate of waste glasses. The increase may occur in the residual glass phase (due to depletion of silica) or in one of the crystalline phases that is formed, like strontium molybdate (Malow, 1967). The increase in leaching of borosilicate waste glasses after devitrification is usually no more than a factor of 2 to 5, although in some instances an increase up to a factor of 10 has been observed in waste glass after maximum devitrification at 750°C as shown in Figure 14. Figure 14 also demonstrates that there can be considerable variation in the leach rate of nondevitrified waste glass.

- (a) There are some exceptions to this statement. Fission product ruthenium and palladium are insoluble in waste glass at all temperatures. The fission product oxide CeO_2 does not completely dissolve in waste glass until a temperature of about 1200°C is reached. Spinel, having the general formula A_2BO_4 , where A can be Fe or Cr and B can be Ni, Zn, Fe(II), etc., apparently may even exhibit a retrograde solubility above 950°C in certain waste glass compositions. Regardless of their high temperature behavior, the effects of these species are indistinguishable from the other devitrification species at the handling and storage temperatures we are concerned with here.

VITREOUS

DEVITRIFIED

FIGURE 13. Photomicrographs of Vitreous and Devitrified Waste Glass

Because the amount and identity of the crystalline species formed during devitrification are so dependent on composition, a large amount of work has been done to identify the various species that may form in specific waste glasses. A review of that work is beyond the scope of this report; however, some general observations may be made:

FIGURE 14. Leach Behavior as a Function of Devitrification for Two Representative Borosilicate Waste Glasses

- The species formed on devitrification of borosilicate waste glasses are often crystalline silicates; boron always remains in the glassy matrix. The end result is a boron-rich residual glassy phase, which has a somewhat higher leach rate than the initial glass due to its higher boron content.
- A larger proportion of the high valence, high atomic weight cationic constituents tend to appear in the crystalline silicate species. Sodium, potassium, and calcium, etc., are relatively absent from the crystalline silicate devitrification species. In general, however, other anions that may be present in the glass, such as molybdate, phosphate, or fluoride, exhibit a strong tendency to form crystalline devitrification species which, in contrast to the silicates, usually preferentially contain alkalis and alkaline earths. The identities of the exact crystalline compounds that will form from a given glass composition cannot yet be predicted with confidence; they must be determined empirically.

- Secondary devitrification reactions have also been observed in which a rapidly-formed crystalline species is slowly converted into another crystalline species.
- At optimum devitrification conditions, crystals may form several hundred micrometers in the longest dimension. Micro-cracking in the surrounding glass matrix may occur, due to mismatching thermal expansion coefficients.

It is apparent that devitrification of waste glasses is a complex phenomenon. Devitrification can be prevented by cooling the glass quickly and subsequently maintaining the glass at temperatures below approximately 500°C. However, the primary concern is: Need devitrification of waste glass be avoided? And the answer seems to be no, based on all available data. The only significant devitrification effect is on leach rate, and the magnitude of this effect can be defined for any given glass with a few simple tests. To date, these tests have always shown no more than a factor of 10 increase in the leach rate of cesium, the radioisotope whose leach rate is most sensitive to devitrification effects. It should be emphasized that if the decision is made to "accept devitrification," only a limited central region (perhaps 20 vol%) of the waste glass in the canister would be affected. The waste glass at the canister wall would remain vitreous because the maximum allowable wall temperature during handling is only 375°C.

A large amount of work is continuing on the devitrification of waste glass. Two areas in particular are receiving attention. More needs to be learned about the location of the actinides in devitrified waste glass. The effects of the nonuniform radiation pattern caused by the possible concentration of some actinides in certain crystalline species are now being measured. Hydrothermal alteration, as opposed to the thermal devitrification discussed so far, is also being studied. Based on analogies with naturally-occurring glasses, the possible enhancement of crystallization by water at geologic storage temperatures is being examined. This topic is discussed more fully in Section 3.4.4.

Phase Separation

Phase separation is another time-temperature dependent phenomenon involving atomic rearrangement. It is a liquid-

liquid phase separation. Borosilicate glasses are particularly susceptible to phase separation, forming a boron-rich and a silica-rich phase (Doremus, 1973). There is evidence that some borosilicate waste glasses are phase separated as formed.

Phase separation is difficult to study because the dimensions of the separated phases are usually less than 500 Å. Figure 15 is a photomicrograph of a typical waste glass illustrating probable phase separation. Two types of phase separation are known in borosilicate glasses. In one the borate-rich phase is distributed as discrete disconnected globules in the silica-rich phase. In the other, the borate-rich globules are connected to form a continuous network. It may be postulated that the former type of phase separation occurs in waste glasses, since if the borate-rich phase was continuous, higher leach rates would be expected than those actually observed.

FIGURE 15. Transmission Electron Micrograph of Phase-Separated Waste Glass

Molybdenum and sulfate also exhibit phase separation in borosilicate waste glasses. A molybdenum-rich salt phase that also contains sodium, cesium, and strontium separates. As is typical of phase separation phenomena, the molybdenum-rich phase is completely miscible in waste glasses above about 1150°C. At lower temperatures the phase separation is composition dependent. If the concentration of molybdenum and sodium is high enough in borosilicate waste glasses, the

molybdenum-rich phase will separate out on a macroscale and float to the surface of the molten glass. As noted on page 17, reducing conditions can be used to avoid the separation of the molybdenum salt phase.

As in the case of molybdenum, sulfate tends to separate as a sodium salt phase, which may also contain other alkali metals, alkaline earths, and chromates. Immiscibility of Na_2SO_4 becomes apparent when the SO_3 content of borosilicate waste glass exceeds 1.2% (DPST, 1976). If the sulfate content is expected to be higher than this, the presence of soluble Na_2SO_4 in the product glass can be prevented by adding reducing agents, such as C, to the melt. Sulfate will then be reduced to gaseous SO_2 at glass melt temperatures. Lead-borosilicate glass compositions have also been described for the immobilization of sulfate-containing radioactive waste (Shukla, 1977).

Phosphate glasses are less susceptible to phase separation. In particular, molybdenum does not separate out in phosphate glasses. The French have developed phospho-silicate glass compositions for the incorporation of very high molybdenum-content radioactive wastes (Bonnland, 1966).

3.4 LEACHING

The known chemical durability of the ancient manmade glasses of the Mesopotamians, Egyptians, Greeks, and Romans for 2000 to 4000 yr, even during immersion in seawater for over 2000 yr in the case of Greek and Roman glasses, was one of the original incentives for developing waste glasses. Following this lead, measurements of leach rate have been key factors in the selection of waste glass compositions.

Intuitively, low leach rates are desirable. Two questions arise, however, in quantifying what is apparent intuitively: 1) How low must the leach rates be? and 2) Can leach rates measured in the laboratory be interpreted and extrapolated to predict long-term behavior in actual geologic situations? The first question is quite complex and is the subject of ongoing risk analyses which are outside the scope of this report. Answering the second question, however, is precisely the ultimate goal of the leach tests that are being made on waste glasses. The answer is not yet complete. The present status of the investigations will be described in the following sections.

Table 4 shows the factors that can significantly effect the value obtained in a given leach rate. Some of these factors are intrinsic, related only to the waste glass itself and its condition. Others are extrinsic; they are external factors which can vary independently of the waste glass. The factors in Table 4 are interrelated. Understanding the leaching of waste glass rests on knowing the type of influence each factor has in relation to the others.

TABLE 4. Factors Affecting Leach Rate Measurements

Intrinsic	Extrinsic
Glass composition	Temperature
Thermal history	Pressure
Radiation effects	Composition of leachant (including pH and Eh)
Physical form	
Surface character	Flow rate of leachant

3.4.1 Mechanisms

The basic mechanisms of glass leaching are well known. Many commercial glass studies have clarified these mechanisms since chemical durability (resistance to leaching) is a fundamental requirement for many commercial glass applications. Although the basic mechanisms are known, understanding of the quantitative effects of the various factors as applied to specific situations is still lacking in many cases.

The primary leaching mechanism below about 80°C is a diffusion-controlled ion exchange in which hydrogen or hydronium ions exchange for cations in the glass lattice. The overall result of this reaction is a depletion of cations from the glass surface leaving a hydrous silica layer, which also contains some slow-diffusing multivalent cations. As this silica-rich surface film develops, it functions as an increasingly protective barrier which progressively slows down the rate of leaching. Finally, the rate of leaching is slowed until a second mechanism assumes the rate-controlling function. The second mechanism is surface corrosion. Surface corrosion refers to erosion of the silica-rich film by a combination of chemical dissolution (the

solubility of silica in deionized water is 18 ppm) and mechanical sloughing-off of hydrous increments of the film. At room temperature, surface corrosion results in a much slower reaction than diffusion, but as the temperature increases, surface corrosion apparently increases at a faster rate than diffusion. At temperatures above about 80°C surface corrosion is usually the controlling mechanism (Zager, 1960).

The following expression is often used to express the leach rate of silicate glasses (Paul, 1977):

$$Q = at^{1/2} + bt$$

where: Q = the quantity of a specific cation that has been removed from the glass

t = the time glass has been in contact with leachant

a, b = constants.

The first term represents the contribution due to diffusion and the second term, that due to surface corrosion.

The foregoing explanation of the mechanisms involved in leaching is based mainly on studies of simple alkali silicate glasses which have leach rates that are high enough to be measured conveniently. Commercial glasses contain constituents added specifically to increase leach resistance, such as alkaline earth and aluminum oxides. These additives increase the chemical durability so much that it is very time-consuming to make measurements to corroborate the leaching mechanisms. Usually accelerating techniques, such as elevated temperatures or high acidity, are resorted to, which complicate interpretation in terms of fundamental mechanisms. Overall, the results indicate that the basic mechanisms inferred from the simple glasses are useful guidelines for interpretation of the data, especially for extrapolation to longer time behavior, but other factors are also involved. A principal factor is composition of the leachant. In actual leaching situations the water in contact with waste glass will be impure because: 1) natural waters contain dissolved ions, and 2) unless the water is moving very rapidly, dissolved ions from the glass will concentrate at the sur-

face. These ions can participate in complex back reactions which usually, but not always, slow the leach rate of the glass (Adams, 1970).

The ultimate conclusion is: In order to evaluate a glass for a specific use, the test program should duplicate as closely as possible the conditions of that use (Bacon, 1968). This is even more true for radioactive waste glasses than for commercial glasses, because of the complexity of the waste glass compositions and their applications.

3.4.2 Techniques for Waste Glass Leach Rate Measurements

The majority of leach rates that have been measured on waste glasses to date have used deionized water that is replenished on a preset schedule. The leach-rate data obtained in this manner serve as an index of relative leach resistance for the comparison of waste glasses. These data can be used to estimate the behavior of waste glass in certain situations, such as: 1) canister failure in a water storage basin, 2) a transportation accident in which the failed canister lands in a river, and 3) even as an upper limit in some geologic repository situations. Leach rate data more pertinent to waste glass behavior in geologic repositories require a closer approximation of repository conditions and are just now beginning to be reported.

Leach tests can be divided into two principal types, dynamic and static.

Dynamic Leach Tests

In dynamic leaching the test specimen is either exposed to flowing leachant, or to aliquots of leachant which are replenished periodically. The goal is to minimize interfering surface reactions; relatively constant dilute conditions are maintained in the leachant contacting the specimen. Dynamic tests furnish data for intercomparison of waste glasses and for evaluation of accident behavior in flowing water. The standard leach test proposed by the IAEA (Hespe, 1971) and the Soxhlet test (Mendel, 1973) are both dynamic tests.

The proposed IAEA test uses waste glass specimens immersed in water at room temperature. The water is removed, analyzed,

and replaced with fresh water at set intervals. The intervals between leachant changes are one day initially, but are gradually increased as the test continues. (a)

In the Soxhlet test the waste glass specimen is contacted with flowing distilled water at a temperature that depends on design of the apparatus, but is usually in the range of 80 to 100°C. Because of the elevated temperatures employed, test results are obtained quickly; duration of the tests is usually 72 hr or less.

Static Leach Tests

In static leach tests the test specimen is exposed to stagnant water. Static leach tests are of most value in evaluating the behavior of waste glass in the event of water intrusion into a waste repository, where the water flow rate would usually be very low. The high temperature-high pressure tests being made with waste glasses are usually static tests. The goal is to determine the final equilibrium state of the system.

Reporting Leach Test Results

Leach tests usually measure either, 1) weight lost by the glass specimen as a function of time, or 2) the concentration in the leachant of one or more of the leached ions as a function of time. If weight loss is measured, the results are reported simply as percent weight loss or as a corrosion rate, penetration depth per unit time. Such results are useful for comparison purposes, but are an oversimplification since congruent corrosion of all waste glass constituents is assumed. In actuality, incongruent leaching always occurs, at least in the initial stages of leaching. Some alkali metal and alkaline earth ions may leach at rates 10 to 100 times faster than cations of higher valence, such as the rare earths. The extent of incongruent leaching can be determined if the concentration of different ions in the leachant is determined. This is the procedure used to obtain fundamental data

which give information about leaching mechanisms. It is the procedure used in the IAEA proposed standard leach test.

The leach rate, as calculated from analysis of the ions in the leachant is usually expressed as follows:

$$L = \frac{a_n W}{A_0 S t_n} = \frac{(b)}{2} \text{ g/cm}^2\text{-day}$$

where: a = amount of a specified isotope leached during the nth leachant renewal period

A = amount of the specific isotope initially present in test specimen

W = weight of test specimen, grams

S = geometrical surface area of test specimen, cm

t = duration of leachant renewal period, days.

The leach rate can also be expressed as a penetration rate, cm/day, which is obtained by dividing L by the density of the glass.

Figure 16 shows the typical range of leach rates obtained for waste glasses when leached according to the IAEA proposed standard leach test (or procedures that have basic resemblances to the IAEA test). An indication is also given of the usually observed relationships in the leach behavior of important radioisotopes. Leach rate is quite dependent on glass composition, but the leach behavior of most waste glasses lies somewhere within the range shown in Figure 16. As Figure 17 shows, the same leach data can be plotted as cumulative penetration, which is sometimes thought to give a more graphic interpretation of what the leach rates mean.

- (a) Users of the proposed IAEA test find that the leach rate they measure is somewhat dependent on the frequency at which the water is changed (Bradley, 1978). The IAEA test is being modified by a working group of the International Standards Organization (ISO) and it will probably be recommended that the frequency of water changes be kept uniform throughout the duration of the test.
- (b) The assumption being made is that all of the glass constituents leach at the same rate as a_n . Of course they do not, thus different leach rates can be obtained for the same glass sample, depending upon which specific isotope is analyzed. The correct way to express a waste glass leach rate is, "g of glass/cm²-day, based on the behavior of ¹³⁷Cs" (or ⁹⁰Sr, or whatever isotope was analyzed in the leachant).

FIGURE 16. Typical Waste Glass Leach Rates

FIGURE 17. Typical Waste Glass Leach Rate Data Expressed as Cumulative Penetration

3.4.3 Effect of Flow Rate and Potential For Back Reactions

Various situations can be hypothesized in which waste glass could come in contact with water. The flow rate of water past the waste glass can vary widely in the hypothesized situations, ranging from the rate of a river running past particles of waste glass to zero flow rate in a repository containing water that never moves. The short-term effect of flow rate is that the leach rate decreases as the flow rate decreases. This is because of "back reactions," including formation of a saturated hydrous film on the surface and even the possible formation of precipitates which protect the surface from further reaction. Such short-term effects are well known in waste glass leaching. Figure 18 shows an example of this effect.

FIGURE 18. Effect of Leachant Flow on Leach Rate

At slower flow rates the pH of the solution in contact with the glass surface rises because hydrogen ions are used up in the leaching reaction. The rate of attack on glass increases significantly when the pH raises above 8.5 to 9.0 (Adams, 1972). An equilibrium pH is observed in commercial glass bottles holding static water that may be as high as 9.5 (Budd, 1961). Similar equilibrium pHs are observed with some waste glasses. Waste glass is being further tested, but present indications are that even though the pH may be quite high, steady-state stagnant systems exhibit very low leach rates.

3.4.4 Effect of Temperature and Pressure

The effect of temperature on leach rate must be considered because the waste glasses may be self-heating to various degrees. The leach rates of commercial glasses increase with temperature, usually by a factor of 10 to 100 for each 100°C increase in temperature (Adams, 1970). Similar increases are observed for waste glasses although the rate of increase tends toward the lower end of the range, i.e., about a factor of 10 for each 100°C increase in temperature (Mendel, 1976).

Leaching temperatures above 100°C could exist in the geologic repository, although it is by no means certain that they will. (While the waste glass is on the surface, the maximum leaching temperature is limited to 100°C by the boiling point of water.) Within a relatively wide latitude the geologic repository can be designed to operate at any temperature desired. Cooling will be by natural conduction after the repository is sealed, and the maximum temperature can be controlled in the following ways:

- The time of repository sealing and natural conductive cooling can be supplemented with convective or forced air cooling until the repository is sealed.
- The heat content of the individual canisters can be limited by a lengthened interim storage period before the waste glass is emplaced in geologic repositories, or by a reduction of the waste loading in canisters of high-heat wastes.
- The dimensions of the storage array can be adjusted. Cooler temperatures can be maintained by spreading out the waste. Storage efficiency can be maintained by interspersing low-heat producing wastes.
- The effective heat transfer can be increased between the waste glass capsule and the host rock. (For instance, wet, rather than dry, conditions will increase heat transfer and thus lower the temperature of the waste.)

The maximum temperature permitted in the repository will be determined through tradeoffs between economics and design or operational difficulties. Minimum cost

would seem to be associated with high waste loading in small mine volumes, but several other factors have to be considered: (a)

- Heat effects must not adversely affect the structural integrity of the mine while portions of it are still being filled and/or occupied by workers.
- Thermal and radiation effects on repository host rocks must be considered, including dehydration, recrystallization, changes in thermal conductivity, and physical strength.
- Thermal expansion must not cause fracturing of either the repository rock, or impervious layers around the repository, which can adversely affect its integrity.
- Reaction rates of water with the host rock and with canisterized waste glass must be considered.

These factors are still being evaluated and the final design temperature of the repositories will not be known until the evaluations are complete. Reaction rates between waste glass and the host rock will be one input to the evaluation.

In autoclave tests, reactions which can be characterized as hydrothermal alteration have been observed with waste glasses above about 150°C. In these reactions, crystalline species are formed at the surface of the glass. The reactions are probably a combination of atomic rearrangement in the leached portions of the glass matrix plus deposition of precipitates formed from leached ions. Potential for the amount and number of latter reactions is greatly enhanced when the waste glass is in contact with a geologic medium, as discussed in Section 3.4.5.

Hydrothermal experiments involving waste glass and candidate geologic hosts, in particular salt, have been underway at PNL for about two years. Most of these tests have been conducted at 250 to 350°C to obtain steady-state conditions rapidly (one to three weeks) at the extreme high end of the potential temperature range. As stated above, the design temperatures for the repository have not been fixed; data obtained in the hydrothermal experiments, and at lower temperatures, will serve as one input factor to the decision

(a) Retrieval considerations will also limit temperature, but it is possible only a limited number of initial canisters will be designed to be retrievable.

on what the design temperature should be. A recent topical report by J. H. Westsik, Jr., and R. P. Turcotte describes the initial PNL hydrothermal tests (Westsik, Jr., 1978). Data in the report demonstrate the following:

- The reaction rate of waste glass and aqueous solutions is a strong function of temperature. This is shown in Figure 19.
- Other "stable" materials, including candidate geologic media, react at rates similar to waste glass in the hydrothermal tests, as Figure 20 illustrates.
- The reaction mechanisms predominant in salt brine are different from those which predominate in pure water.

FIGURE 19. Effect of Temperature on HLM Glass Leach Rates in Salt Brine and De-ionized Water

FIGURE 20. Comparative Leach Rates of Several Materials in Salt Brine at 250°C

Figure 21, a and b, shows that reaction with the glass is slower in salt brine than in water perhaps because of decreased H^+ activity in salt brine. However, the ions which are released from the glass tend to stay in solution in salt brine because of chloride complexing, whereas in pure water they tend to recombine to form new crystalline compounds. Identification of the new crystalline compounds is just beginning.

The preliminary conclusion is that until the hydrothermal reactions are understood in more detail, they should be minimized, since both the geologic host rocks and the waste glass can be significantly altered. (a) The reactions can be minimized if only small amounts of water are present while the repository is hot, or if the repository temperature never exceeds a certain predetermined limit, or if a multiple barrier system is used which prevents water from contacting the waste for several hundred years.

3.4.5 Effect of Leaching Media

Leaching media that need to be considered in evaluating the leach resistance of

- (a) The discussion has disregarded the presence of the canister. This is a conservatism, since it is probable that canisters of present design will provide a significant barrier. (See comparative corrosion rates in Figure 20). If the canisters were designed especially for this service, different materials of construction would probably be used, such as titanium.

FIGURE 21. Cross Sections of Waste Glass After Exposure to Salt Brine and Deionized Water for 1 wk at 350°C

waste glass fall into three major classifications, as shown in Table 5.

Even though the variations possible in classifications 2 and 3 are very large, prohibiting experimental testing of all the possibilities, it is important to note that in the tests performed to date with various waste glasses, the leach rates measured in deionized water have always been equal to or higher than those measured in classification 2 or 3 media. (a) This is apparently due to back reactions of the type discussed in Section 3.4.3. It may be concluded that the leach rates measured with the Soxhlet test and the proposed IAEA standard test, using deionized water, yield conservative results. They represent probable maximum leach rates. This conclusion is born out by the results of Canadian tests (Merritt, 1977), which are the only experience to date with the *in situ* contact of waste glass with natural water.

In the Canadian tests, waste glass was buried approximately 10 to 12 ft underground in a swampy portion of the Chalk River nuclear reservation in 1960. The flow rate of groundwater past the buried waste glass waste was measured to be 200 ft/yr by a tritium inoculation technique. The groundwater downstream of the waste glass has been monitored for ^{90}Sr since the burial. The leach rate calculated from the groundwater samples had decreased to 5×10^{-11} g glass/cm²-day by 1968 and has remained at that low rate since. This leach rate is a factor of 10^3 - 10^6 lower than that measured on waste glasses in dynamic laboratory leach tests, such as the proposed IAEA standard test. In fact, the initial leach rate of the Canadian glass, as measured in the laboratory, was approximately 1×10^{-5} g glass/cm²-day (Merritt, 1977). It appears that in the actual geologic exposure system, a relatively stagnant layer of naturally occurring and leached ions

(a) An exception may be very low pH natural waters, known to occur, but which have not yet been tested as leachants for waste glass. The effect of pH on waste glass leaching is discussed on page 42.

TABLE 5. Potential Leaching Media for Waste Glasses

Classification	Potential Method of Encountering Media	Possible Variations in Media
1. Deionized water	Canister leak in water basin	Minor
2. Nonsaline natural water	Canister failure during a transportation accident. Disposal in a nonsalt geologic repository. ^(a)	Large major variables are pH, Eh, carbonate-bicarbonate, sulfate, calcium, and chloride (minor concentrations of chloride are ubiquitous in nature)
3. Saline natural water	Disposal in a salt repository or in seabed ^(a)	Large major variables are pH, Eh, sodium, magnesium, and sulfate

(a) Canister failure by corrosion is assumed to occur within a finite time.

exists around the glass blocks, which is inhibiting further leaching to a very low rate.

Effect of pH

Most natural waters have a pH between 4 and 9. The pH of the solution in contact with waste glass is frequently increased by the leaching reaction to approximately pH 9, the highest pH extreme observed in nature. Therefore, high pH natural waters are not a concern since they do not appreciably change the conditions that would normally arise at the surface of waste glass being leached. In extreme cases, acidic natural waters can potentially have a significant effect. At pH 4, the leach rate of most waste glasses is increased only slightly over that at pH 7, but at pH 3 the increases can be a factor of 2 to 10, or even more, depending on the glass formulation (Ross, 1978).

Borosilicate waste glasses are appreciably soluble in mineral acids (1 to 6 N) because of their relative low silica content. Their solubility in mineral acids is possibly advantageous because it assures that the solidification can be reversed if, at any time in the future, it is desired to change the waste form or extract some component of the waste which has become valuable.

Effect of Salt Brine

Deep salt deposits which underlay extensive areas in many parts of the world are

leading candidates for the location of final disposal sites for nuclear waste. They are obviously free of moving water, otherwise the salt would have migrated away as saline water long ago. Salt deposits do contain small amounts of stagnant waters as saturated salt brine. The total water content is usually less than 0.5% by weight. Most of the brine is in small "bubbles" occluded in the salt crystals. The brine bubbles will migrate toward heat sources because the crystalline salt is more soluble on the warm side of the bubble than on the colder side. Thus canisters of waste buried in salt formations may partially, at least, contact brine solution. It has been estimated that a maximum of 30% of brine could migrate to any given canister (Jenks, 1972). (Significant amounts of this brine may evaporate when the repository is ventilated during filling.)

More tests are being made, but the tests made thus far indicate that the leach rate of waste glass at 25°C in salt brine, or in more dilute salt water, such as seawater, is up to a factor of 10 less than the leach rate of the same glass in deionized water. Leach rates at elevated temperatures may be more pertinent since some exposure of the waste glass to salt brine is expected to occur while the repository is still at an elevated temperature. This is because rapid stress corrosion cracking that will fully penetrate the walls of the canisters is expected to occur only a few months after waste burial. Autoclave experiments are being carried

out at elevated temperatures to evaluate the behavior in these circumstances (Westsik, Jr., 1978).

Effect of Nonsaline Geologic Waters

Other potential geologies being considered for disposal of nuclear waste include granite, basalt, and shale formations. These differ from salt formations because the chemical and physical makeup of the geology is more complex and larger amounts of water can conceptually be present. Examination of the potential interactions between waste glass and these geologies is less advanced than it is with salt; only limited data has been reported (McCarthy, 1978). However, based on available data, it is expected the leach rates of waste glass in these natural waters will be lower than the leach rate of the same waste glass in deionized water. Thus the results obtained with deionized water yield conservative results when applied to the analysis of nonsaline geologic repositories. Hydrothermal reactions between waste glass and nonsaline repository materials are also being studied (McCarthy, 1978).

3.4.6 Extrapolation of Leach Data - Fitting to Models

It is not practical to run leach tests for longer than a few months, or perhaps a few years--tests for process control purposes should not take more than a few days--yet leaching behavior over much longer periods should be understood. The periods of concern correspond to the lifetimes of the radioisotopes in the waste. Therefore, mathematical models, based on postulated mechanisms and observed behavior, are being developed to extrapolate expected leach behavior to times beyond which it can be experimentally verified.

Factors which should be treated in leaching models are represented graphically in Figure 22. The location and shape of line AB is determined by the leaching mechanism, and represents leaching from a semi-infinite medium. The location and shape of line AC is very dependent on temperature and leaching media. It is important to realize that even though line AB cannot be totally verified, it is possible to verify the portion AA' within experimentally practical times, and thus establish the major behavior pattern with good confidence. Line AC represents leaching from a finite medium. Models should be able to predict releases from different sizes (and configurations) of initial

FIGURE 22. Considerations in Modeling Long-Term Leaching

waste forms. In addition, models should factor in radioactive decay, as represented by line AD. A final refinement would factor in the effect of leachant velocity. Leaching is suppressed by a low leachant flow. THE LOW FLOW SITUATION, PROBABLY MOST REPRESENTATIVE OF A GEOLOGIC REPOSITORY, WOULD BE REPRESENTED BY LINE AE.

Several models have been proposed for extrapolating the leach behavior of solidified radioactive waste forms, including glass. Most include the effects of radioactive decay and specimen size. None include the refinement of factoring in the effect of flow rate. This may be very difficult. Efforts to do it for minerals being leached by groundwater have not been successful (Paces, 1973).

A review of the various proposed leaching models is beyond the scope of this report. The interested reader is directed to the following list of references:

- Griffing, 1974
- Cohen, 1977
- Moore, 1977
- Godbee, 1974
- Logan, 1977

Kottwitz, 1974
Anders, 1978
Ewest, 1976.

Of course, leaching is only part of the story; it only provides the source term. What leaching means in terms of hazard to man requires pathway analysis. This is discussed further in Section 4.

3.5 RADIATION EFFECTS

Perhaps the most unique feature of waste glass is the high levels of contained radioactivity potentially possible. Depending on the type and amount of radioactivity incorporated in waste glass, the total beta-gamma dose to the glass may reach 10^{12} rads in the first one thousand years; the alpha events due to decay of the contained actinides, many of which have long half-lives, may exceed $10^{19}/\text{cm}^3$ of glass in 250,000 years.

Will self-radiation for thousands of years change the properties of waste glass in any way, making the assumptions concerning the glass used in various long-term behavior analyses invalid? It must be proven that, once the thermal and hydrothermal devitrification effects are defined, the glass will no longer change, and that long-term radiation effects can be discounted. With some reservations, described in the following sections, all evidence indicates that it is indeed legitimate to discount radiation effects. The evidence shows waste glass to be very radiation-resistant material.

Radiation can potentially cause:

- stored energy buildup
- bulk or localized density changes
- changes in rates of devitrification
- amorphization of crystalline species (metamictization)
- changes in mechanical strength
- changes in leach rate
- helium buildup (from alpha decay).

The effects can be due to the energetics of the decay event itself or, in some cases, to the fact that the alpha and beta decays transmute one element into another which may have a different valence, ionic radius, and chemical behavior.

Although the list of possible radiation effects is long, the tests performed to date have revealed no effects which would jeopardize the use of glass for the long-term immobilization of up to at least 1×10^5 Ci of fission products per liter of glass and 1×10^3 Ci of actinides per liter of glass.

Most radiation effects are temperature-sensitive; most of the effects diminish as temperature increases. This means that there is an inverse time relationship between the thermal effects and the radiation effects. Whereas the potential for thermal effects is only in the early life of the waste glass, the potential for radiation effects reaches a maximum in the later life of the waste glass, when it is completely cool.

3.5.1 Comparison of Types of Radiation and Experimental Techniques

Waste glass will be subjected to a mixture of gamma, beta, neutron, and alpha radiation. Except for the associated heat generation, the effects of gamma and beta radiation on waste glass are minimal. This is according to theory and was demonstrated in the WSEP program. The WSEP waste glasses received doses up to 5×10^{11} R with little effect. The contained isotope responsible for the major portion of the doses received by the WSEP waste glasses was $^{144}\text{Ce-Pr}$, a combined beta-gamma emitter. Neutrons also contribute little to the potential radiation damage mechanisms for waste glass, because the neutron flux associated with α -n reactions and spontaneous fission is comparatively low (Newman, 1973). The alpha particles from decay of the actinides, and particularly the recoil particles associated with alpha decay, have the major potential for creating radiation effects in waste glass (Jenks, 1973). Therefore, it is the effects of actinides in waste glass that are receiving emphasis in studies being conducted at several sites in the U.S. and elsewhere.

The actinide content of waste glass is made up of a mixture of uranium, neptunium, plutonium, americium, and curium isotopes, plus their decay products. The relative amounts of the actinides in a waste glass depends on the source of the radioactive waste incorporated in the waste glass. In all cases, however, the actinide alpha-decay effects will continue for long times. Table 6 lists the alpha decays during the first million years for one representative waste glass.

TABLE 6. Time Distribution of Alpha Decay in a Representative Waste Glass

Time of Vitrification	Alpha Events, Percent of Total
First 100 yr	3.4
100-1,000 yr	3.4
1,000-10,000 yr	6.8
10,000-100,000 yr	16.7
100,000-1,000,000 yr	69.7

It is apparent that the effects of the actinides cannot be studied when glasses are simply prepared with representative actinide concentrations. The doses achieved in practical experimental times would be relatively insignificant in terms of the overall dose, so techniques to accelerate the effects must be used.

Two basic accelerating techniques are available: external bombardment and internal bombardment. External bombardment with protons, alpha particles, or heavier particles can yield a very high dose rapidly, but since the effects are concentrated in a surface layer less than 100 μ m deep, they are difficult to interpret. Fast neutron bombardment can give "knock on" particles with effects somewhat analogous to alpha recoil particles, but quantification of the effects is difficult because of the assumptions that must be made. Slow neutron bombardment can be used to give high energy fission fragments internally, but again somewhat tenuous assumptions have to be made to interpret the results. The conclusion is that the most realistic simulation of the actual situation is accomplished by internal bombardment using alpha decay. This is the approach that has been used in most waste glass studies.

Alpha effects are accelerated experimentally by preparing waste glasses containing actinide isotopes with short half-lives. Isotopes which have been used include ^{238}Pu ($t_{1/2} = 87$ yr), ^{242}Cm ($t_{1/2} = 162$ days), and ^{244}Cm ($t_{1/2} = 18$ yr). The question then arises: What total dose is required in the accelerated experiments? The answer is simplified, because radiation effects tend to reach an equilibrium or saturation value, which changes very little with additional radiation doses. Thus for many of the effects, the goal can be simply to define the saturation values. The saturation doses can then be related to the doses expected in waste glass.

Representative doses have been calculated and reported (Mendel, 1977). The cumulative alpha dose in glasses containing once-through LWR fuel cycle waste and full-recycle LWR fuel cycle waste will be about 3×10^{18} and 3×10^{19} α/g , respectively, after 100,000 yr. Experiments have shown that most of the radiation effects reach an equilibrium, or saturation value, which is relatively independent of waste glass composition (Ross, 1978). However, the dose required to saturate different property effects does vary. For instance, density change saturation rates at less than 2×10^{18} α/g , whereas stored energy does not saturate until the cumulative dose is about 4×10^{18} α/g . It has been calculated that a cumulative dose of 1.26×10^{19} α/g is required to achieve saturation radiation effects, i.e., full metamictization, of naturally-occurring zircon (Bursill, 1966). (Metamictization will be discussed further in Section 3.5.4.) Cumulative dose rates exceeding 1×10^{19} α/g of glass have been achieved in a waste glass at PNL which contains 8 wt% ^{244}Cm (Ross, 1978). Other specimens have been prepared containing 1 and 3 wt% ^{244}Cm so that dose rate correlations can be made. No dose rate effects have been found, giving confidence that the results obtained in the accelerated tests are valid and can be used to predict the radiation effects on waste glasses many years into the future.

The radiation effects described in the upcoming sections were all determined using internal bombardment techniques, i.e., actinide doping. They are considered valid with one reservation. In the tests to date, the actinides have been fairly uniformly distributed in the glass matrix. In devitrified waste glass, particularly, it is conceptually possible that the actinides could become concentrated to form localized areas with higher dose rates than the surrounding glass. It has already been determined that this does not occur with curium. The behavior of other actinides in devitrified glass is still being evaluated.

3.5.2 Stored Energy

Stored energy is latent energy stored in a substance by radiation-induced displacement of atoms from their normal lattice position. The latent energy is released as heat when the temperature of the substance is raised sufficiently. The specific heat of waste glasses is usually about 0.2 cal/ $^{\circ}\text{C}\cdot\text{g}$. The maximum stored energies in waste glasses are in the range of 30 to 60 cal/g, thus under adiabatic

conditions, the maximum additional temperature rise that could occur due to rapid release of the stored energy is only 150 to 300°C. It may be concluded that the stored energy levels in waste glass are not a hazard.

Stored energy buildup is an inverse function of temperature, as shown in Figure 23a. Figure 23b shows that the release of stored energy is fairly uniform over a temperature range from 150°C up to the softening point of the glass, at which temperature all of the stored energy has been released. The formation of stored energy reaches an equilibrium value at 25°C after an integrated dose of less than 4×10^{18} α/g of glass, as shown in Figure 23c.

The data shown in Figures 23a, 23b, and 23c were obtained on a specific zinc borosilicate waste glass composition using 1 and 8 wt% ²⁴⁴Cm. Stored energy measurements on other waste glasses have yielded similar results within a factor of 2 to 3 (Ross, 1978; Scheffler, 1977). The differences are attributed to compositional effects.

3.5.3 Density Change

Density change is a commonly observed radiation effect in ceramic substances. The density changes observed in waste glasses, which are a maximum of about 1%, are much smaller than those observed in some very stable ceramic materials. Density changes of 14% occur in irradiated crystalline silica (Lell, 1966) and 8% in irradiated alumina (Clinard, 1975).

The density change in waste glass reaches an equilibrium value after about 2×10^{18} α/g. Only minor density fluctuations occur with further increases in radiation dose.

As shown in Figure 24 density change in waste glass can be positive or negative; the glasses can either shrink or swell. The direction of the density change is apparently a function of composition. Conceptually, it may be possible to formulate waste glasses that exhibit no density change.

Two potential effects of radiation-induced density change need to be evaluated: 1) possible canister strain, and 2) possible stresses in the glass which will cause some spontaneous fracturing. Tests indicate that neither effect is likely to cause problems. Increased

canister strain results only with glass formulations where density decreases with radiation. At the maximum density decrease observed of 1%, the circumference of a 12-in.-dia canister would be increased about 1/4 in., a strain readily accommodated by the canister metal. The potential for spontaneous fracturing is greatest in devitrified glass. No radiation-induced cracking has been observed in devitrified ²⁴⁴Cm-doped waste glasses. The investigations are continuing.

3.5.4 Radiation Effects on Devitrification and Metamictization

Radiation seems to have little effect on thermal devitrification of waste glasses. Neither the species of devitrification crystals formed nor their rate of formation is believed to be significantly altered. Specimens of four different PNL glass compositions have been prepared with full levels of radioactivity. Similar specimens, but with nonradioactive isotopes of the fission products and chemical stand-ins (rare earths) for the actinides, have also been prepared. The nonradioactive and radioactive specimens have been subjected to the same thermal devitrification conditions. Preliminary results confirm expectations; devitrification behavior is similar. Radiation would not be expected to affect thermal devitrification since radiation effects are annealed out at the temperatures where the devitrification rate is significant (above 500°C).

Over the long term, however, radiation can potentially be expected to affect some crystals in thermally-devitrified glass. This conclusion is based on evidence from the metamict minerals. Metamict minerals are naturally-occurring minerals which, when examined by x-ray diffraction, are found to be amorphous (Pabst, 1952). When heated they release stored energy and become crystalline. The metamict minerals were probably originally crystalline and became amorphous over many millions of years due to radiation effects from small amounts of contained uranium and/or thorium. This is why over the long term, the contained radioactivity in waste glass may tend to reverse devitrification by converting some crystalline phases back to an amorphous glass-like state.

3.5.5 Radiation Effects on Leach Rates

Leach tests made on waste glasses containing up to 9×10^4 Ci/l of fission products are not more than a factor of two higher than those made on nonradioactive

FIGURE 23. Stored Energy in Waste Glass

FIGURE 24. Radiation-Induced Density Change in Waste Glass

simulated waste glasses of the same general chemical composition (Mendel, 1972; Mendel, 1973). This difference is within the normal experimental deviation of leach test data. Similarly, the leach rate of a ^{244}Cm -spiked waste glass was not significantly different from the leach rate of a comparable nonradioactive glass after a cumulative dose over 3×10^{17} α disintegrations/g (Mendel, 1977). Thus radiation does not affect the leach rate of waste glasses, and leach data obtained on non-radioactive simulated waste glass can be used to predict the leaching behavior of fully radioactive waste glass. Tests are producing more data which confirm this conclusion.

In some instances, the internal surfaces of glass vessels containing highly alpha-active solutions have become crazed and have even begun to slough off flakes of surface material (Tuck, 1964). In those cases, the actinide concentrations in solution have been high ($>3 \times 10^{-4}$ Ci/ml), probably higher than would exist in any solution likely to contact waste glass, even after prolonged static contact. This is an area that needs further investigation, although the effect is not thought to have an important impact even if it occurs. For instance, Scheffler et al. studied waste glasses having an abnormally high plutonium content (2 wt%) and observed a periodic sloughing off of a hydrous silica-rich surface layer (Scheffler,

1977). Even so, the leach rate was low, less than 1×10^{-7} g of glass/cm²-day at 25°C. The small amount of plutonium leached could be filtered; it was evidently tightly bonded to hydrous silica particles.

3.5.6 Helium Behavior

Helium atoms are generated wherever alpha decay events occur in waste glass. Each alpha particle captures two electrons to become a helium atom. Helium is slightly soluble in glass; helium also diffuses through glass quite readily. The diffusion is retarded as the glass composition increases in complexity; thus, helium diffusion in waste glass is lower than in quartz glass or commercial soda-lime-silica glass (Turcotte, 1976). Figure 25 shows that the diffusion of a portion of the helium produced by alpha decay is also further inhibited, when compared to that of helium implanted in the glass by solubility at high temperatures. The inhibition is attributed to trapping of some of the alpha-produced helium at point defects. Expressions for both untrapped (D_u) and trapped (D_t) helium diffusion coefficients have been experimentally derived (Turcotte, 1976):

$$D_u = 2.1 \times 10^{-3} \exp(-15,000/RT) \text{ cm}^2/\text{sec},$$

$$D_t = 1.7 \times 10^{-4} \exp(-15,000/RT) \text{ cm}^2/\text{sec}.$$

FIGURE 25. Isothermal Helium Release from Glass

Using these diffusion coefficients, canister pressurization was estimated at two temperatures, 25 and 300°C, as a function of time for waste glass containing LWR once-through and full recycle wastes. The estimated pressures are plotted in Figure 26a and 26b. The solid lines represent no trapped helium, the shaded portion below the lines represents the potential effect of trapped helium. A 10 vol% plenum in the canister and 30 wt% waste loading in the glass was assumed.

Defense waste glasses are not shown in the figures since their helium generation rate is orders of magnitude below that of the LWR fuel cycle waste glasses. The important point is that helium pressurization is negligible even in LWR waste glass canisters; only in the unlikely event that the full recycle waste glass canisters will still be at 300°C after 100 yr, could the pressure reach 150 psig.

3.5.7 Transmutation

Radioactive decay results in the transmutation of the decaying isotope, often to atoms of significantly different valence and ionic radius. Some of the transmutations that occur in waste glass are shown in Table 7. Intralanthanide and actinide transmutations are not shown because the resultant changes are insignificant. The actual number of transmutations that will occur in a given waste glass depends on the fission product loading and the age of the waste when the glass is made. Even in

TABLE 7. Radioactive Decay Transmutations Which Occur in Waste Glass^(a)

Initial Ion	Transmuted Ion
Cs+1	Ba+2
Tc+7	Ru+4
Sr+2	Zr+4
Zr+4	Nb+5
Ru+4	Pd+2
Pd+0	Ag+0

(a) Actinide and lanthanide transmutations are not shown because resulting effects are small.

glasses with a high waste loading, the total number of nonoxygen atoms undergoing transmutations will not exceed 2%. Because of the nonstoichiometric nature of the glass, it is expected that the transmutations can be accommodated without effect. The exception may be severely devitrified glass, because the effect of transmutation on the stability of crystals could be more severe.

a. Once-Through

b. Full Recycle

FIGURE 26. Potential Helium Pressure in Waste Glass Canisters

INTRODUCTION

FORMATION OF RADIOACTIVE WASTE GLASS

PROPERTIES OF RADIOACTIVE WASTE GLASS IN CANISTERS

STABILITY OF CANISTERIZED RADIOACTIVE WASTE GLASS DURING HANDLING, STORAGE AND FINAL ISOLATION

THE STABILITY OF CANISTERIZED WASTE GLASS
PROVIDES EXCELLENT BACKUP IN OUR MULTIBARRIER
WASTE MANAGEMENT SYSTEM, HELPING TO ASSURE
MINIMUM IMPACT ON FUTURE GENERATIONS

FIGURE 27. Prototypical Waste Glass Canisters Prepared in the PNL Non-radioactive Waste Vitrification Pilot Plant

FIGURE 28. Engineered Storage Facility for Waste Glass Canisters at the AVM Facility, Marcoule, France

4.0 STABILITY OF CANISTERIZED RADIOACTIVE WASTE GLASS DURING HANDLING, STORAGE, AND ISOLATION

The stability of canisterized waste glass is a key factor in nuclear waste management because the waste glass contains most of the initial radioactive inventory.(a) Prototypical waste glass canisters prepared in the PNL waste vitrification pilot plants are shown in Figure 27. The storage facility for the waste glass canisters prepared in the French AVM facility is shown in Figure 28.

The system has redundant protection designed into each waste management step; thus, canisterized waste glass is only one part of the overall containment system. Until the waste is emplaced in geologic isolation the properties of the canisterized waste form become important only in highly unlikely accident situations; they are the ultimate backup barrier assuring that no harmful release of activity can occur.

The function changes somewhat in geologic isolation. Initially, at least, it is planned that for a period of several years the waste can be retrieved relatively easily from the repository. During this period, the waste glass still serves only as a backup barrier, important only in highly unlikely accident situations. Finally, however, long-term geologic isolation must be considered. At some time during this period, it is possible that water may collect or intrude into the repository, that the canisters may corrode, and that the controlled release of radioisotopes from the waste glass into the water can become a functional part of the waste management system.

Risk analysis is being used to evaluate the overall effectiveness of the waste containment system. Risk can be defined as:

$$R = P \times C$$

where: R = risk,

P = probability of a certain event occurring, and

C = consequences of that event.

Risk analysis involves summarizing the individual risks, after each has been quantified as much as possible.

The stability of the waste form serves as a primary input used to quantify C, the consequences of each event. In waste management systems analyses, C is usually expressed as a radiation dose to an individual or a representative population. The radiation dose is proportional to the activity released. Since the initial release has to be from the primary waste form, the waste glass properties described in Section 3.0 have a major effect on most consequences.

The remainder of this report concerns the effects of waste glass properties on releases in various postulated events. All risk analyses(b) agree that only three routes for releases need be considered to evaluate the radiological consequences of waste management:

- (a) It is noteworthy that after a few hundred years most of the fission products will have decayed. Then actinide activity becomes dominant. The actinide content of the combined nonhigh-level wastes is comparable to that of high-level waste. For this reason research and development activities are under way to make available techniques for incorporating these wastes in glass also (MLM, 1976; Ziegler, 1977; Kupfer, 1976).
- (b) Details concerning risk analyses are outside the scope of this report. Readers desiring more information on risk analyses pertaining to radioactive waste management are directed to the following references: Kimmel, 1976; Center, 1976; Wingender, 1978; Brucher, 1978; Burkholder, 1976; Logan, 1974.

- radioactive vapor
- radioactive respirable particles (aerosols)
- radioactive water.

Releases via these routes can be converted into radiation doses by pathway analyses.

To estimate the potential magnitude of the releases, the individual steps in the waste management system have to be defined. Since waste management procedures are still evolving the steps can be described only in general terms, but these descriptions are sufficient to understand the protective role played by canisterized waste glass.

4.1 TYPICAL SCENARIOS FOR PROCESSING, HANDLING, STORAGE, AND DISPOSAL

The AVM plant at Marcoule in southern France is achieving routine radioactive operation this year. This is the first waste glass plant to be put in routine operation and may be considered prototypical of others that will follow. The AVM is located in a separate building dedicated solely to the manufacture of canisterized waste glass. The waste glass is manufactured remotely in a heavily-shielded cell using automatic equipment, master-slave manipulators, and overhead cranes. The cell is remotely maintained.

The canisters are decontaminated and removed remotely from the cell to an adjacent air-cooled interim storage cell, below ground level in the same building. Additional interim storage space can be added to the building as required. The recently-announced Swedish plan is also for air-cooled, dry interim storage of waste glass canisters for at least 30 yr (Wivstad, 1978). Water cooling, however, is more efficient and can be used for wastes with a higher radioactive heat generation rate. Water cooling has generally been assumed to be preferable for interim storage of power reactor wastes in the U.S.

The length of time the waste glass canisters are in interim storage may vary from a few days to many years. In the U.S., for nongovernmental HLW glass, the limit is 10 yr, as set forth in 10 CFR 50, Appendix F. In other countries, interim storage times as long as 200 yr are being considered. In all cases, however, interim storage, as the name implies, is not permanent and the waste will be trans-

ferred to another site for permanent isolation. Deep (>2000 ft) geologic repositories have been determined to be acceptable options for permanent isolation; many nations are researching these repositories.

The U.S. is developing a geologic repository in salt and investigating other potential sites for geologic repositories in basalt, granite, and clay formations. In Germany, low-level radioactive wastes have been placed in an abandoned salt mine at Asse since 1967; intermediate-level wastes are also being disposed of in the Asse mine.

Geologic repositories will probably service several waste generation sites, at least some of which may be located considerable distances from the repository site. Therefore, most waste management scenarios include a transportation step. Waste management is made more efficient if transportation of the waste is minimized. For instance, the proposed reprocessing plant at Gorleben in Germany is located directly above a proposed salt repository so that no off-site transportation of waste will be required. Similarly, isolation of Hanford wastes in the massive basalt formations that underlie the Hanford site is being studied.

From the foregoing, it can be seen that although differing in details, most waste management scenarios consist of the same four steps:

- processing and inplant post-treatment
- interim storage onsite
- transportation
- geologic isolation.

4.2 PROCESSING AND INPLANT POST TREATMENT

A generic inplant processing cell for the manufacture of canisterized waste glass is shown in Figure 29. The protective barriers for the waste include:

- glass
- canister (In most processes, there will be a short time in a separate glass melter during which times the melter is also a barrier.)
- hot cell (and associated ventilation system)

FIGURE 29. Protective Barriers for HLW During Processing and Inplant Post-Treatment

- process building (and associated ventilation system) plus surrounding isolation area.

It is sometimes suggested that the relatively high temperatures involved in waste glass processing may enhance potential for release of radioactive volatiles or aerosols. This is not true. Such releases are prevented by the design of the processing and off-gas treatment equipment. The equipment is operated at a negative pressure in relation to the cell atmosphere. All gases from the processing equipment go through a series of condensers, scrubbers, and HEPA filters before they are released to the atmosphere. Experience in the WSEP program, where glass containing megacuries of activity was melted at temperatures up to 1200°C (McElroy, 1972), plus detailed safety analyses, have shown that the routine releases from a waste vitrification facility are only a fraction of those associated with a reprocessing plant. Both releases are well below established limits (Bodkes, 1976; CWMS, 1978).

Analyses have also shown that accidents cannot cause high releases. The safety analyses indicate that the most serious

accidents that could occur in the solidification processing cell are not glass-related. Instead they are potential accidents in the offgas system, fire in the HEPA filter banks or condenser failure, or overpressure leading to rupture of a calciner (Brucher, 1978; CWMS, 1978). The releases of even these low probability accidents are within acceptable limits.

Although extremely unlikely, accidents involving impact (dropping or bumping canisters) can be envisioned. The impact tests performed on simulated waste canisters at PNL demonstrated that the canisters can withstand much larger impacts than they can possibly be subjected to in the processing cell. Impact velocities in the processing cell are limited by the size of the cell. Canisters will not be able to fall more than 15 to 20 ft.

4.3 INTERIM STORAGE

The two generic interim storage options, air-cooled and water-cooled, for waste glass canisters are shown in Figures 30 and 31. The protective barriers for the waste include:

FIGURE 30. Protective Barriers for HLW During Interim Storage in Air

FIGURE 31. Protective Barriers for HLW During Interim Storage in Water

Air-Cooled Storage

- glass
- canister
- heavy shielding
- facility building and surrounding isolation area

Water-Cooled Storage

- glass
- canister
- 15 ft of water
- facility building and surrounding isolation area

Potential release mechanisms will be considered in design and operation of the interim storage facility, thus releases of any kind are very improbable. The release mechanisms that will be guarded against include: 1) canister corrosion which exposes waste glass; 2) impact, causing canister leak, and 3) overheating, causing

canister failure. Even in the event release from a canister occurs by any of these mechanisms, the other barriers shown in Figure 30 and 31 act to mitigate the effects.

4.3.1 Canister Corrosion

Canister corrosion is not a factor in air-cooled storage, for two reasons. First, stainless steel has excellent corrosion resistance in air. Second, even if corrosion exposed a small amount of waste glass, the radioactivity release through volatility would be well below permissible limits because of the relatively low temperature (<375°C) at the glass surface.

Canister cracking via intergranular corrosion, although infrequent, may occur in water basin storage. When a canister begins to leak because of corrosion, it will be removed from the basin, dried out, and overpacked. Before it is removed, some activity will leach into the basin water. In fact, the increased activity in the water will alert the water basin operators to the leak. The activity level in the water will be controlled by water purification equipment routinely operating at the basin (Figure 31). When the canister is removed, this equipment will restore the basin water to its original activity.

4.3.2 Impact, Causing Canister Leak

No impacts which would cause a canister to leak appear possible during interim storage. A drop of 30 ft barely dents a waste glass canister. Free falls of over 15 to 20 ft are not possible during interim storage because of the facility design.

4.3.3 Overheating, Causing Canister Failure

The canisters can overheat if coolant flows are restricted or stopped. The flow restriction would not cause much overheating (<375°C maximum) in an air-cooled interim storage facility, because these facilities are not designed to accept canisters which could cause a higher temperature rise. Furthermore, the facilities are designed to assure natural convective air flow in the event of loss of forced cooling.

Water-cooled basins would be used for storage of canisters with larger heat generation rates. In these basins, prolonged loss of coolant flow could cause the basin water to boil and evaporate. Even with canisters generating 20 kW of self-heat, it would take six to seven days for all of the water to evaporate (ARHCo, 1973). Since there would be backup systems which could be placed in service to supply cooling water, total loss of water is very unlikely. But if it did occur, the close packing of the dry canisters would result in a further rise in the temperature of the canisters. The most severe possible consequences would be that a few of the canisters would fail, due to one or more of the following causes: 1) internal pressurization, 2) internal corrosion of the canister by molten glass, or 3) yielding or melting of the canister wall at the hottest point.

Internal pressurization would be unlikely to cause canister failure because of the relatively large vapor space in the canister and the relative absence of volatiles. In some cases, helium might be a factor in pressure buildup. However, because of the relatively short duration probable for interim storage, in most cases the total helium inventory will not have become large enough to cause much pressure. In any event, whether the failure is due to pressurization which allows vapor to escape, or to a larger failure which allows molten glass to escape, the release mechanism for radioactivity would be volatilization. Complex heat transfer analyses would be required to estimate the temperatures which could occur. The volatilization rate is controlled by temperature as described in Section 3.3.1. It is unlikely that the temperatures could ever reach that required for significant volatilization to occur.

Loss of water from a water basin, which would allow overheating to the extent discussed above, is almost incredible. Water basins for interim storage of canisterized waste glass are of the same standard design that is used for storage of spent fuel. In fact, the same storage pool would probably be used for both purposes at a commercial reprocessing plant. Backup methods of maintaining the cooling water supply are included in design of the basins.

4.4 TRANSPORTATION

A generic transportation system for canisterized waste glass is shown in Figure 32. During transportation, the protective barriers for the waste include:

- glass
- canister
- shipping cask (The cask is loaded and unloaded remotely in heavily shielded cells or under water, which provides an additional protective barrier during these steps.)

The shipping casks would be similar to casks that have been used for over 10 yr with a perfect safety record for the shipping of spent reactor fuel on public railroads and highways. These casks must meet stringent regulations before they are licensed. Recent tests at Sandia have further demonstrated the totality of protection provided by these shipping casks

FIGURE 32. Protective Barriers for HLM During Transportation

(Yoshimura, 1978). Shipping casks were smashed into a massive concrete barrier at 80 mph and engulfed in high temperature fires. The integrity of the casks was not breached; none of the liquid placed in the casks to monitor for leaks escaped.

Shipping casks will not contain more than about nine canisters (Perona, 1972). Notwithstanding the apparent impregnability of the shipping cask, and the additional impact-resistant barrier provided by the canister, accidents in which waste glass particles are released probably cannot be totally discounted. In this event, some respirable particulates would be released. Other particles, which were not dispersed in the air but which did escape from the canister, would present a cleanup problem. Before the cleanup was completed, there might be some rainfall; because railroads and highways tend to follow water courses, the particles might initially be scattered in a stream or river. In these cases, the leach rate of the glass becomes important. Some risk analyses have concluded that transportation of waste glass has the greatest potential for accidental release of any waste management step (Cohen, 1977). The risks are quite similar to those encountered in shipping spent fuel, an operation that has been proven very safe, both in practice and in safety analyses.

4.5 GEOLOGIC DISPOSAL

A generic geologic disposal operation is shown in Figure 33. The protective barriers for the waste include:

- canister (The complete protection provided by the canister is temporary. Due to intergranular attack, it is assumed cracks that penetrate the wall will form within a few months in salt, within a few years in other geologies. Even though cracked, the canisters will continue to cover most of the glass surface and thus will provide partial protection for much longer periods.)
- overpack (Optional. In some instances overpacks may be used to guarantee that the canisters can be retrieved from the repository for a specified length of time, probably in the range of 5 to 50 yr. Engineered barriers can be designed for a much longer useful life, e.g., the Swedish 1000-yr life concept.) (Mivstad, 1978)
- artificial geology (Optional. The repository may be backfilled with a material with special properties, a highly adsorbent or a highly impermeable material, for instance.)
- the natural geology.

It is only in geologic isolation that the system is designed to allow potential releases from the waste glass. This is because it is believed impractical to try to assure that water will not at some future time reach the waste glass. When it does, leaching reactions will result in release of some activity.(a)

(a) All substances leach to a certain degree. Even SiO_2 , the major constituent of beach sand, has a measurable solubility in water (Barnes, 1967).

FIGURE 33. Protective Barriers for HLW During Geologic Disposal

The formations chosen as locations for geologic repositories will be selected so that even if some activity is released from the waste form, the activity can never reach the biosphere in harmful concentrations. The major factors providing this assurance are: 1) the selection of geologic sites with as low as possible potential for water flow, 2) the long tortuous pathway that water must take from the repository to reach the biosphere,^(a) and 3) the natural adsorptive or ion exchange capacity of minerals and soil for most of the long-lived radioisotopes in fission reactor wastes. The controlled release of

the radioisotopes, provided by the inertness of the glass gives an additional safety factor.

In assessing the overall potential for releases during the life of the repositories, three periods must be considered:

- The operational period. This period includes the operations of receipt of the canisters, emplacement of the canisters, possible retrieval operations, backfilling, sealing, and decommissioning of the repository.

(a) As has been noted elsewhere, "The potential exposures from disposed radioactive waste can occur either from the waste migrating from its disposal location into man's environment or it can occur from individuals encountering the waste" (Adams, 1978). A basic precept of deep geologic isolation of canisterized HLW glass is that the latter type of exposure, through well drilling, mining, etc., is automatically minimized by the location 2000 ft underground.

- The self-heating period. Depending on the initial heat loading and the geology (and what temperature is chosen as the end of the self-heating period), this period starts before the operational period ends and may last for hundreds or even thousands of years.
- The perpetual isolation period. This is an open-ended period; analyses are still being made to determine the length of the significant time period, but it is probably about 100,000 yr. Many investigators have pointed out that the hazards associated with high-level waste repositories decrease with time. After ^{137}Cs and ^{90}Sr decay, the remaining hazard is of a relatively low magnitude which is well within man's ordinary experience (Bell, 1971; Hamstra, 1975; Haug, 1976; Tonnesson, 1977; Gera, 1977). As shown in Figure 34, after a few thousand years, the total activity in a repository will be less than the activity in a similar volume of uranium ore. This calculation is based on the volume of a repository in which the canisters are positioned 33 feet apart. Figure 34 also shows that the hazard potential of the repository is much less than that of some other types of ore bodies. The comparisons are based on total available hazards potential, either radiological or chemical. They put the hazards associated with the disposal of high-level waste in perspective; they do not however, address how the pathways to man compare. These studies are still underway for nuclear waste.

4.5.1 The Operational Period

Repository operations on the surface are similar to many of those discussed in Section 4.3 because there will be a small interim or lag storage facility at the repository into which shipping casks will be unloaded. Canister handling may include decontamination, installation of overpacks, and other hot-cell operations. During these surface operations, the waste glass serves as an ultimate release barrier that will be needed only in the event of almost incredible accidents.

Emplacement of the waste glass canisters involves new and undemonstrated operations. In particular, the canisters must be lowered down a shaft which may be 2000 ft or more deep.^(a) The repository design will include redundant safety fea-

FIGURE 34. Toxicity of Nuclear Waste Over Time Relative to That of Average Mineral Ores of Toxic Element

tures to prevent accidental dropping of the canisters. The extremely remote possibility of a long drop remains, however, in which case the impact data from Figure 10 are pertinent. Breaking of the canister with the release of a fraction of contained glass, which did not occur in tests simulating 120 ft/sec impacts, could possibly occur in such a drop although impact velocities in excess of 120 ft/sec are very unlikely because impact-damping devices will probably be part of the shaft design. During the operational period, the ventilation air will be filtered. A breached canister in the repository would delay operations and require costly clean-up, however, there would be negligible release of activity to the environment.

Retrieval operations, if required, would necessitate lifting the canisters back up a shaft. Canisters designed for retrieval will probably be overpacked; thus another layer of protection would be added and releases would be even more unlikely in the case of a retrieval accident.

The last step in the operational period of a geologic repository will be decommissioning. Decommissioning will convert the repository from a storage mode to a disposal mode. The repository and its access and ventilation shafts will probably be completely backfilled. In addition to the backfill, special seals will be installed in the shafts. The aim of decommissioning is to prepare the repository for its ultimate purpose: to maintain isolation of the contained radioactivity without further surveillance by man.

(a) The Germans expect to begin lowering drums of intermediate-level waste down a 3000-ft shaft at the Asse salt mine in 1979 (Kuhn, 1978).

4.5.2 The Self-Heating Period

The maximum temperature in a repository, which will probably be reached approximately 50 yr after start of filling, will be controlled by regulating the amount and distribution of radioactive decay heat placed in the storage array of canisters. Currently, it is expected the maximum temperature of the wall of the canister will not be allowed to exceed 150 to 200°C.^(a) These temperatures will not cause devitrification, even if the time at temperature is several decades. The question becomes more complex when the possibility of canister failure, accompanied by the ingress of water, is considered.

Salt Repositories

Salt deposits in the U.S. where repositories may be located can contain about 0.5 wt% saturated salt brine, present as small spherical inclusions in some of the salt crystals. Some or all of the water in this brine may evaporate and be removed as water vapor in the ventilation air during the operational phase of the repository. Nevertheless, residual hot brine can be expected to cause corrosion of the stainless steel canisters. Thus, some waste glass may be exposed to residual hot salt brine within a few months or years after emplacement of the canisters.^(b) The most severe conditions, however, cannot occur until after the repository is completely backfilled and sealed. Then it is expected that because of the plasticity of salt, lithostatic pressure will develop rapidly. This, coupled with the impermeability of compressed salt, may cause the waste glass to be exposed to salt brine solutions at temperatures of up to 150°C and 2,000 psi.

The hydrothermal conditions that may exist around the canisters in a salt repository can result in rapid attack on the waste glass and may even produce some new crystalline species at the waste glass-salt interface. The extent of the attack, however, will be limited by the amount of water present in the brine. It is probable that as the available brine solution

(no more than 30%) becomes saturated with leached glass constituents, an equilibrium will be approached and attack on the glass will stop. More experiments are required for complete definition of the final result but it will probably be that a pocket of contaminated brine will exist in the vicinity of each glass block. But each glass block will still contain over 99% of the total activity. Release of more activity from the waste glass would require that the saturated brine be replaced with fresh unsaturated brine. This cannot occur unless immense amounts of impermeable salt surrounding the waste glass are first dissolved. Such dissolution is extremely improbable as demonstrated by the survival of the present salt beds for more than 100 million years. This self-evident proof of permanence is a major reason that salt is a primary choice for the location of geologic repositories in the U.S. and Germany.

Non-Salt Repositories

The siting of geologic repositories in massive basalt, granite, and shale formations is also being considered. The potential for the presence of much larger quantities of water which can be flowing, although slowly, makes analysis of the expected behavior of canisterized waste glass in these types of repositories much different than that in salt repositories. Because of their plasticity, shale deposits probably occupy an intermediate position midway between salt and the crystalline basalts and granites.

Unlike salt, the alternative geologic formations have no mechanism to draw water to the hot canisters. In addition, the sites in these formations will be specially selected for their isolation from known aquifers. Nevertheless, the intrusion of at least some water through cracks, joints, and fissures must be accepted. Therefore, it is assumed that nonsalt repositories will be flooded with water at sometime after they are sealed. Different predictions, ranging from decades to milleniums, have been made as to how long it will be after backfilling

(a) The temperature which will be allowed in repositories is still under study.

(b) It is expected that at least during initial operation of the repository, storage sleeves, or overpacks made of brine-corrosion resistant materials will be used to protect the stainless steel canisters assuring their retrievability.

before the canisters become surrounded by water. Analysis of the very-near field effects^(a) upon ingress of water in a nonsalt repository is a complex function of many variables:

- rate and severity of intergranular corrosion of the canisters (how quickly and how much of the glass surface is exposed)
- temperature of the water (or steam) in contact with the glass
- quantity and rate of water flow in contact with the glass
- chemistry of the water in contact with the glass
- composition of the backfill material in contact with the canister.

These variables are site-specific and will have to be analyzed for each individual geologic repository site. However, the effects of temperature and water flow, probably the two most important variables, can be treated generically to some extent.

The optimum design temperature for nonsalt repositories is still under investigation; one consideration in the repository design will be an assessment of the magnitude and importance of "waste-rock" interactions, which are really waste-water reactions. Corrosion and alteration of waste glass by water are strong functions of temperature. Studies are only in the preliminary stages, but it is apparent that if water contacts waste glass at 150 to 200°C, for instance, a layer of glass 1 cm deep could possibly be leached within 1 to 10 years (Figure 19).

The question then becomes: what happens to the radionuclides that are leached? Some chemical recombination to stable crystalline phases can be expected. But some radionuclides will also be available for migration. For these the rate of flow of the water becomes important. Computer-modeling techniques have been used to examine the effect of flowrate on migration (OECD, 1977). The migration of a given radionuclide is equal to the ground-

water velocity divided by the retardation factor. For instance, a radionuclide with a retardation factor of 10^4 will move only 10 cm when the groundwater moves 1 km. Computer migration models suggest that retardation and dispersion will be effective controls on radionuclides reaching the biosphere (Isherwood, 1978; Grimwood, 1978; Hebel, 1977). Some studies have concluded that because of the effectiveness of these controls, the leach rate of the waste in the repository is of little consequence. For instance, one study compared two very different waste solubilities--in one case the waste was totally dissolved in 0.01 yr and in the other 10,000 yr--and concluded, "It can be seen that little difference in individual dose results over this broad range of solubilities" (Center, 1976).

The models, however, require more refinement and better input data before they can be relied upon completely. In the interim, the inertness of waste glass should be utilized as much as possible. Methods of doing this during the self-heating period (by minimizing the amount of water present and/or temperature control) were described earlier (page 39).

If the temperature of the waste glass in the nonsalt repositories is not allowed to exceed approximately 100°C, the leach resistance of the waste glass will act to limit the rate of release of activity, even if there is a considerable flow of water through the repository. The dynamic leach tests that are routinely used to evaluate waste glasses give data directly applicable to this situation.

4.5.3 The Perpetual Isolation Period

The perpetual isolation period begins after the radioactive heat generation in the repository has decayed to insignificance. From then on, the only unusual effect which may occur will be due to the alpha activity in the waste glass. As described in Section 3.5, it is possible to simulate radiation doses in test specimens similar to those the waste glass will receive in perpetual isolation. Waste glasses have been subjected to radiation

(a) Very-near field refers to the immediate area at the interface between canister and backfill. The additional terms, near field and far field, are used for the entire volume of host rock in the repository, and for the surrounding geologic formations, respectively. Reactions in the very-near field may be thought of as sources of radioactivity which can potentially migrate to the near and far fields, where the radioisotopes are subject to adsorption and ion exchange reactions that retard their migration.

doses equivalent to over 10^5 yr storage at PNL without any important changes occurring.

Leaching will occur during the perpetual storage period and the effects of this leaching are less easy to predict. The three major considerations from the standpoint of the reactions at the glass surface are: 1) the state of the glass surface, particularly if it has been exposed to water during the self-heating period, 2) the effects of the constituents in the natural waters, and 3) the flow rate of the water through the repository.

Two other considerations are important. First, since the beginning of the perpetual isolation period roughly corresponds to the time when ^{137}Cs and ^{90}Sr have decayed to insignificance, the radioisotopes remaining are mainly actinides, which exhibit lower leach rates than ^{137}Cs and ^{90}Sr which dominate during the self-heating period. Second, even though the waste is no longer self-heating, the temperature will still be 40 to 50°C because that is the ambient temperature at the depths planned for repositories.

Leach rates at 40 to 50°C are two to four times higher than those measured at 25°C. After this correction is made, the dynamic leach rates measured at 25°C (Figure 16) can be used to estimate long-term leach behavior in repositories. These estimates indicate that for glass containing fractures at 2-in. intervals less than 1% of the long-lived activity would be released per thousand years.

Estimates of long-term releases involve many variables, including assumptions con-

cerning the leaching mechanism, surface area, and water flow. Investigations are continuing which will increase knowledge concerning the effect of these variables. A goal will be to do experiments which simulate repository conditions as closely as possible. The Canadian burial experiment clearly shows the importance of simulating actual conditions (Merritt, 1976). The leach rates measured from the Canadian blocks of glass buried in the soil at Chalk River have reached an equilibrium value that is orders of magnitude lower than would have been estimated from the standard leach tests done in the laboratory.

The Canadian experiments, plus the decreased leach rate observed in static tests, plus the fact that dynamic tests performed with natural brines or salt brine are usually lower than those measured in deionized water, all give confidence that extrapolations made using the results of standard tests, such as that proposed by the IAEA, will be conservative, i.e., overstate the potential releases. As our understanding increases, we will be able to predict releases more accurately, and it is probable that the more accurate predictions will be for releases of much less than 1% per thousand years.

The conclusion is that waste glass can control the long-term release in the repository to a low rate. The radioisotopes which are released will adsorb strongly on rock or soil particles and thus migrate very slowly. Salt repositories are expected to remain sealed systems during the perpetual isolation period, and there should be no release to the adjoining rocks and salt.

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