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**A Program Plan for Comprehensive
Characterization of Solidified
High-Level Wastes**

December 1975

**Prepared for the U.S. Energy
Research and Development Administration
under Contract E(45-1):1830**

MASTER

Battelle

Pacific Northwest Laboratories

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A PROGRAM PLAN FOR COMPREHENSIVE
CHARACTERIZATION OF SOLIDIFIED
HIGH-LEVEL WASTES

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ABSTRACT

An experimental plan is described for in-depth characterization of canistered solidified waste forms for the storage and disposal of high-level radioactive wastes. The plan is being considered for silicate glass forms at PNL. The basic aspects of the plan have general application and can be applied to other candidate waste forms as well.

The plan is designed to define the behavior of waste canisters and their contents during anticipated handling, storage and disposal regimes. Particular emphasis is placed on long-term thermal and radiation effects.

A 10-year period is projected for complete characterization of any one basic type of waste form, e.g., silicate glass cast in metal canisters. A preponderance of the laboratory effort occurs in the first 5 years. It is assumed that shortly thereafter an operating solidification plant will be available, so that much of the second 5 years can be devoted to corroborative tests made on representative canisters of actual high-level waste. Man power requirements are estimated at 65 scientist man-years during the first 5 years and 30 scientist man-years during the second 5 years.

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A PROGRAM PLAN FOR COMPREHENSIVE CHARACTERIZATION OF SOLIDIFIED HIGH-LEVEL WASTE

J. E. Mendel

1.0 INTRODUCTION

United States policy is to convert high-level radioactive wastes, generated in the reprocessing of spent power reactor fuel, to a "dry solid" which is "chemically, thermally, and radiolytically stable."⁽¹⁾ In order to fully characterize glass as a solidified high-level waste form a comprehensive characterization program plan has been developed. The characterization program plan is also applicable to other potential "dry solid" waste forms.

Selection of the optimum "dry solid" waste form will be based on a combination of considerations, including processing reliability, economics and safety. Within practical limits the latter consideration should assume most importance. A significant aspect of safety is the ability of the waste form, due to its innate properties, to maintain the radioactivity immobilized in any credible situation. The waste form characterization plan which is the subject of this document describes a program to quantitatively measure the innate properties of the waste forms, and determine how they are affected by processing parameters and by thermal and radiation effects during storage and disposal.

2.0 OBJECTIVE OF THE PROGRAM PLAN

The objective of the program plan is to assure that the characteristics of the solidified waste forms are understood so thoroughly that, when the waste forms are put away in interim storage or terminal storage, there will be full confidence that their properties are known, and that any changes or interactions with their environment which may occur later are wholly predictable.

3.0 SCOPE OF THE PROGRAM PLAN

The waste forms considered are those which are proposed for the immobilization of high-level waste from the reprocessing of spent power reactor fuels (and any other wastes which may ultimately be combined with the high-level wastes).

Initial utilization of the characterization plan will be at the Pacific Northwest Laboratory for in-depth characterization of the silicate glasses being developed for in-can melting processes.

Although initially directed toward glass waste forms the plan will be general enough to serve as a model which can be adapted for the characterization of other waste forms, thus facilitating, (1) meaningful comparisons between presently developed waste forms, and (2) quantitative evaluations of future potential advances in waste form quality.

The canister is considered an integral part of the waste form, thus the impact of canister design and potential canister/solidified waste interactions are included in the plan.

Characterization will include optimal waste form specimens prepared under carefully controlled conditions, but will also include engineering-scale specimens prepared under practical conditions representative of routine operation in a production facility.

4.0 SUMMARY OF THE PROGRAM PLAN

Two precursors were needed in order to develop the detailed program plan. First it was necessary to define the properties which had to be measured, and the factors which could influence these properties. Second, the type of experimental specimens that could be made available upon which to make the measurements had to be defined. The program plan then consists of itemizing which desired properties should be determined on what specimens.

4.1 Definition of Properties To Be Measured

A reference matrix was developed which lists properties which should be measured to completely characterize the behavior of a candidate waste form during processing, storage and disposal. Each of the properties may be significantly influenced by the procedures used in processing and handling, and by the resulting thermal and radiation history, hence the need for a matrix. The matrix is a convenient method of illustrating which factors in the production and handling of the waste form may potentially influence a specific property. Development of the matrix is described in Section 6.

4.2 Definition of Experimental Specimens Available for Characterization Measurements

The types of experimental waste form specimens which are being used for characterization measurements are described in Section 7. These range from small-scale nonradioactive specimens with several chemical substitutions for expensive fission product elements, used for screening tests, to engineering-scale specimens made from actual high-level waste in an operating plant. Considerations of availability, cost, convenience of experimental measurements, etc., dictate that several different kinds of specimens be utilized in the detailed characterization of any given waste form.

4.3 Obtaining the Experimental Data

The experimental data which must be obtained to adequately characterize a waste form include the following:

Corrosion of containment (internal and external)

Leachability (dynamic system)

Leachability (static system)

Phase characterization (including devitrification^(a) effects)

Density

Viscosity^(a)

Volatility

Radiation effects

Helium behavior

Thermal conductivity

Thermal expansion coefficient

Electrical conductivity^(a)

Frangibility (mechanical shock, thermal shock and induced stress)

(a) Data pertinent to glass waste form only.

The program plan is expedited by dividing the data collection into two types, formulation dependent and generic. It is necessary to screen a large number of possible glass formulations and to determine the effects of many potential waste composition variations. As described in Section 8, the data collected in these formulation dependent investigations is limited; generic investigations are used for the in-depth characterizations. In the generic investigations, a class (genus) of waste form is assumed to behave in a relatively similar manner, so that a detailed definition of the behavior of one characteristic formulation within the class can be extrapolated to other formulations within the class with few additional experiments. The experimental load is decreased by treating as many properties as possible as generic.

4.4 Additional Necessary Elements of the Program Plan

The program plan includes other necessary elements, which complement the fundamental goal of measuring the pertinent waste form properties.

a. Formulation Development. In-depth characterization of the waste form will be preceded by sufficient formulation development to assure that the more time-consuming and costly characterizations are done only on the formulations most representative of the given waste form.

b. Information Correlation and Dissemination. A fundamental obligation of the program is to make information on waste forms readily available. This will be accomplished by issuing periodic reports devoted exclusively to waste form characterization.

c. Development of Standard Tests. Standard tests that can be applied uniformly to various waste forms are needed for intra- and interlaboratory comparisons of waste form properties and for potential use by the regulatory agency to demonstrate conformance to established specifications.

5.0 PRESENT LEVEL OF UNDERSTANDING

Solidified forms for high-level wastes have been under development for almost 20 years in the U.S. and several foreign countries. A large amount of information on the properties of various solidified waste forms has been accumulated as a result of these development projects. The voluminous information is scattered widely in periodic reports, symposia papers and topical reports. A series of bibliographies of the literature on waste processing and disposal have been issued.⁽²⁾ As an indication of the volume of work being done in this area the bibliography for just one typical year, 1972, contains 464 references.

A diversity of waste form compositions have been examined with little uniformity in measurement techniques. Thus while a large amount of waste form property data have been amassed, the data collection to date may be characterized as extensive, rather than intensive.

Plants for immobilizing high-level waste as a glass form are scheduled to start up in Europe in the late 1970's; the first U.S. waste immobilization facility, producing a waste form yet to be selected, will probably come on line in the early 1980's. Therefore, the time is at hand to switch from extensive to intensive characterization of the waste forms. The goal of this document is to outline the intensive characterization program which is required.

6.0 REFERENCE MATRIX FOR WASTE FORM CHARACTERIZATION

A reference matrix has been developed to assist in bringing structure and order to the many elements which must be considered in the characterization program. The reference matrix (Figure 6.1) assures comprehensiveness by listing all of the properties which must be measured and relating them to the factors which can have influence on them. Thus the waste form characteristics are treated as dependent variables which, as the matrix shows, can potentially be affected by a large number of independent variables.

6.1 The Independent Variables

The independent variables include the key source terms: waste form composition, radiation dose, temperature, time and environment.

The magnitude of the characterization program is controlled to a large extent by the many variations in the independent variables which may occur. None of the independent variables are completely defined at this stage in the development of high-level waste immobilization, thus several levels of each independent variable must be considered. In fact, more rigorous definitions of many of the independent variables will be done only after the results of the characterization program are available, so it is very important that the correct range be chosen for each independent variable.

6.1.1 Waste Form Composition

The waste form composition consists of three components, all of which are variable:

1. High-level waste composition
2. Composition and amount of additive used to convert high-level waste to nondispersible form
3. Design, and material of construction, of canister used to contain solidified waste during handling and storage.

PROPERTIES OF WASTE FORM AFFECTING POTENTIAL FOR DISPERSION OF CONTAINED RADIOACTIVITY VIA AIR OR WATER			DEPENDENT VARIABLES		INDEPENDENT VARIABLES		INFORMATION NECESSARY TO DEFINE SOURCE TERM																																																																																																																																																																																																																																																																																																																																																																																																														
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							RADIOACTIVE INVENTORY IN WASTE	NOT RADIOACTIVE CONSTITUENTS OF WASTE											ADDITIVE COMPOSITION	ADDITIVE: WASTE RATIO	PROCESS EQUIPMENT, MATERIAL OF CONSTRUCTION	TEMPERATURE	TIME AT TEMPERATURE	RATE OF COOLING	AGITATION (WHERE APPLICABLE)	CANISTER MATERIAL	COOLING MEDIUM	THERMAL HISTORY	TIME	TEMPERATURE TRANSIENTS	IMPACT ENERGY	SURROUNDING MEDIA	TIME IN CONTACT WITH MEDIA	TIME	THERMAL HISTORY	STORAGE MEDIUM, AT CONTACT	STORAGE MEDIUM, LONG RANGE																																																																																																																																																																																																																																																																																																																																																																																
ENVIRONMENTAL REACTIONS		CORROSION OF CONTAINMENT (EXTERNAL)	☐	☐	☐	☐	☐	☐	☐	☐	☐	☐	☐	☐	☐	☐	☐	☐	☐	☐	☐	☐	☐	☐	☐	☐	☐	☐	☐	☐	☐	☐	☐	☐	☐	☐	☐	☐	☐	☐	☐	☐	☐	☐	☐	☐	☐	☐	☐	☐	☐	☐	☐	☐	☐	☐	☐	☐	☐	☐	☐	☐	☐	☐	☐	☐	☐	☐	☐	☐	☐	☐	☐	☐	☐	☐	☐	☐	☐	☐	☐	☐	☐	☐	☐	☐	☐	☐	☐	☐	☐	☐	☐	☐	☐	☐	☐	☐	☐	☐	☐	☐	☐	☐	☐	☐	☐	☐	☐	☐	☐	☐	☐	☐	☐	☐	☐	☐	☐	☐	☐	☐	☐	☐	☐	☐	☐	☐	☐	☐	☐	☐	☐	☐	☐	☐	☐	☐	☐	☐	☐	☐	☐	☐	☐	☐	☐	☐	☐	☐	☐	☐	☐	☐	☐	☐	☐	☐	☐	☐	☐	☐	☐	☐	☐	☐	☐	☐	☐	☐	☐	☐	☐	☐	☐	☐	☐	☐	☐	☐	☐	☐	☐	☐	☐	☐	☐	☐	☐	☐	☐	☐	☐	☐	☐	☐	☐	☐	☐	☐	☐	☐	☐	☐	☐	☐	☐	☐	☐	☐	☐	☐	☐	☐	☐	☐	☐	☐	☐	☐	☐	☐	☐	☐	☐	☐	☐	☐	☐	☐	☐	☐	☐	☐	☐	☐	☐	☐	☐	☐	☐	☐	☐	☐	☐	☐	☐	☐	☐	☐	☐	☐	☐	☐	☐	☐	☐	☐	☐	☐	☐	☐	☐	☐	☐	☐	☐	☐	☐	☐	☐	☐	☐	☐	☐	☐	☐	☐	☐	☐	☐	☐	☐	☐	☐	☐	☐	☐	☐	☐	☐	☐	☐	☐	☐	☐	☐	☐	☐	☐	☐	☐	☐	☐	☐	☐	☐	☐	☐	☐	☐	☐	☐	☐	☐	☐	☐	☐	☐	☐	☐	☐	☐	☐	☐	☐	☐	☐	☐	☐	☐	☐	☐	☐	☐	☐	☐	☐	☐	☐	☐	☐	☐	☐	☐	☐	☐	☐	☐	☐	☐	☐	☐	☐	☐	☐	☐	☐	☐	☐	☐	☐	☐	☐	☐	☐	☐	☐	☐	☐	☐	☐	☐	☐	☐	☐	☐	☐	☐	☐	☐	☐	☐	☐	☐	☐	☐	☐	☐	☐	☐	☐	☐	☐	☐	☐	☐	☐	☐	☐	☐	☐	☐	☐	☐

(1) PHENOMENA CAUSED EXCLUSIVELY BY RADIATION (RADIATION WILL ALSO HAVE A CONTRIBUTING INFLUENCE ON MOST OTHER WASTE FORM PROPERTIES TO A DEGREE DEFINED BY THE WASTE COMPOSITION AND OTHER INDEPENDENT VARIABLES).

FIGURE 6.1. Reference Matrix for Waste Form Characterization

6.1.1.1 High-Level Waste

High-level waste consists mainly of the aqueous raffinate from the first cycle of a Purex solvent extraction process, but other miscellaneous waste streams may be contained with the high-level waste. Due to differences in Purex flowsheets and the types and quantities of miscellaneous wastes which may be included, a significant variation in waste composition can occur. These variations must be factored into the program. Examples of typical high-level waste compositions are given in References 3, 4 and 5.

6.1.1.2 Additives Used to Convert High-Level Waste to Nondispersible Form

Up to the present time the largest effort on low dispersible waste forms has been devoted to the development of glass forms. In order to produce glasses with the required properties the glass-making additives often comprise 60 to 75% by weight of the final waste forms and introduce new elements not present in the initial waste.

Other waste forms are also being developed, some of which are heterogeneous within the canister, being made up of increments of the primary waste form embedded in a matrix of metal or other materials. For the heterogeneous waste forms the characterization program must also define how potential interactions between the component parts affect waste form behavior.

6.1.1.3 Canister

Present plans are that, following solidification, the high-level waste will be sealed in metal canisters for convenience and added safety during subsequent storage, handling, and ultimate disposal. Most of the canister development to date has utilized 304L stainless steel as the material of construction, however there are several other candidate materials under consideration.

Many of the canister design details are still under development also. The maximum outside dimensions will probably be limited by regulations to about 2 ft in diameter by 15 ft long but smaller canisters will be acceptable

and may prove more desirable. Examples of canister design modifications under consideration include the use of internal cooling fins and "over packing," i.e., recanning the canisters.

6.1.2 Radiation Dose

The radiation dose received by the waste form is dependent on many factors. Some examples of the factors are:

1. Type of fuel elements reprocessed
2. Irradiation history of fuel elements
3. Time since reactor discharge
4. Efficiency of solvent extraction (determines actinide loss to waste)
5. Composition of waste form (controls specific activity, potential for α -n and n- α reactions, heterogeneity of isotope dispersion etc.)
6. Waste form geometry
7. Environment (proximity to other canisters, neutron reflection and moderation).

Theoretical considerations indicate that the actinides are the major source of potential radiation damage, thus it is most important to know their concentration and distribution in the waste form. The identity and quantity of actinides and fission products present in the irradiated fuel elements can be obtained from computer codes such as ORIGEN.^(6,7)

6.1.3 Temperature, Time and Environment

The conditions to which the waste form will be exposed in a typical handling sequence representative of current U.S. planning are shown in Table 6.1. Some of the steps in the sequence shown in Table 6.1, e.g., retrievable storage and perhaps transportation, may be omitted, as procedures for high-level waste handling are finalized, or retrievable storage and terminal storage may turn out to be one and the same. The characterization program must be flexible enough to encompass these and other options.

TABLE 6.1. Representative Conditions to Which the High-Level Waste Form May Be Subjected

	Potential Handling Sequence	Potential Temperature Range, °C ^(a)	Probable Time Span	Probable Environment
<u>Processing Conditions</u>	Processing Post-processing ^(b)	50-1400 50-800	<1 week <1 month	Dynamic heating and cooling (hot cell) Dynamic heating and cooling (hot cell)
<u>Storage and Transport Conditions</u>	Interim Storage Transportation Retrievable Storage	50-800 50-800 -20-600	<30 years <6 weeks <100 years	Dynamic cooling (water basin) Shipping cask Static cooling (air convection)
<u>Accident Conditions</u>	Accident/Recovery ^(c) Nonretrievable Debris ^(c)	50-1000 Ambient	<8 weeks ∞	Uncontrolled, in man's biosphere Uncontrolled, in man's biosphere
<u>Disposal Conditions</u>	Transportation Terminal Storage	0-100 0-300	<6 weeks ∞	Shipping cask Uncontrolled, remote from man

(a) Includes surface and centerline extremes.

(b) Includes weighing canister, welding on canister lid, canister decontamination, and nondestructive testing, such as ultrasonic scanning, leak checking, radiation profilometry and calorimetry.

(c) Nonroutine, included for safety analysis.

Safety analyses of waste handling will include all credible accident situations which can occur at any time during the sequence. The behavior of the waste form during accidents should be predictable. Accident situations are divided into two aspects in Table 6.1. First, during the accident and the recovery operations relatively large quantities of waste form may exist without controlled cooling, and high temperatures may result. Second, depending on the location and magnitude of the accident, some of the waste form may be nonretrievable. The nonretrievable portion of the waste form may be assumed to consist of extremely small particles, thus self-heating will not be a factor.

6.1.3.1 Temperature

A considerable amount of the engineering required in the handling of high-level waste is concerned with assuring that provisions are available for properly controlling the temperature of the waste at all times. The maximum allowable temperatures which should be tolerated during processing and storage are still being defined. Results of the waste form characterization will greatly assist in this definition. Therefore it is important that the entire range of possible temperatures be included in the initial program.

Except for the short time during processing when the temperature will be raised purposely to remove thermally unstable constituents, the waste form thermal conditions will be a combined function of the self-heating due to radioactive decay and the engineered cooling provided to counteract this effect. Self-heating sufficient to make cooling requirements a significant consideration will persist for a long time, as may be seen from the heat generation calculated for a typical high-level waste in Table 6.2.

The temperature of the waste form at any given time will be a function of many factors, including:

1. Type of fuel elements reprocessed
2. Irradiation history of fuel elements
3. Time since reactor discharge
4. Efficiency of solvent extraction (determines actinide loss to waste)

5. Composition and physical state of waste form (determines waste loading thermal conductivity)
6. Canister design (diameter, cooling fins, if any, etc.)
7. Degree of contact between waste form and canister
8. Environment (engineered and natural cooling).

There will be a thermal gradient across the waste form due to the self heating. Computer codes are available which will predict the temperature profiles in waste forms as functions of the above factors. It is too early to restrict the waste form characterization to any one thermal history however. Instead the full range of potential temperatures shown in Table 6.1 should be considered.

An important factor in many thermal effects considerations, particularly in accident situations, is rate of change of temperature. This factor is discussed further in the following section.

TABLE 6.2. Thermal Power and Radioactivity in Typical High-Level Waste

Age, Years After Reprocessing	Waste from Reprocessing 1 Metric Ton of Irradiated Fuel (a)	
	Watts	Curies
1	8,090	1,690,000
10	1,090	320,000
100	115	35,400
500	4.3	227
1,000	2.72	116
10,000	0.785	34.6
100,000	0.0696	16.4
1,000,000	0.0299	3.93

(a) Reactor power = 30 MW/MT, exposure = 33,000 MWd/MT, 0.5% fuel loss to waste, reprocessed 150 days out-of-reactor.

6.1.3.2 Time

Some representative time periods, which are of individual interest during the sequence of waste handling steps, are shown in Table 6.1. Not only the duration of these time intervals but the dynamics of the transfer from one step to another will have potential effects on waste form properties.

Each of the time intervals shown in Table 6.1 represents an individual operation. While the waste form is in that operation, temperature changes should be only a function of the decay rate of the radioactive isotopes present, and thus relatively slow. The cooling will be engineered to assure that the shortest aged material within the operation does not exceed the design temperatures.

Transfer from one operation to another will involve moving from one cooling system to another, however. Thermal transients which are difficult to predict may very well occur. Thus the characterization program must include determination of the effects of rapid heating and cooling rates upon the waste form.

6.1.3.3 Environment

The waste form environment serves two functions:

1. It provides additional barriers to the release of radioactivity.
2. It provides a heat sink for radioactive decay heat.

During the early years in the life of the waste form, the environment must be specially designed to provide shielding and heat removal. Heat removal requirements become negligible after about 500 years and massive shielding is no longer required (Table 6.2). The principal function of the environment then becomes one of minimizing mobility of isotopes.

As shown in Table 6.1, representative environments can be defined for processing, storage and transport of the waste forms. The environments during accident conditions can only be postulated. Many locations for terminal storage of the waste forms are under active investigation, ranging from bedded salt deposits to sites at the bottom of the ocean.

6.2 The Dependent Variables

The dependent variables listed in the reference matrix (Figure 6.1) define the potential for dispersion of the waste form via air or water. Determination of the properties permits a quantitative estimation of the countermeasures to dispersion provided by the waste form.

The dependence of the waste form properties upon certain independent variables is indicated by open circles in the reference matrix. Thus density, for instance, is mainly affected by waste form composition, thermal history and radiation dose (defined by initial waste composition and age). There may also be apparent interactions between dependent variables. For example, changes in density may be accompanied by concomitant changes in leach rate, or induced stresses which affect physical strength. The underlying source of the changes in leach rate or physical strength, however, will have been the independent variables of thermal history and radiation dose. Full use of the reference matrix can assure that related changes in all of the dependent variables are known for any set of independent variables.

The dependent variables are arranged in five groups in the reference matrix. The groups are listed in order of their approximate relative importance:

1. Environmental Reactions

Includes the properties that determine the waterborne dispersion potential of a given waste form.

2. Thermal Stability

Includes the properties that are strongly influenced by temperature.

3. Radiation Effects

Includes the properties wholly due to radiation (radiation will of course affect other properties, but only as one of several influences).

4. Bulk Properties

Includes the properties that must be known to design and operate the waste form manufacturing process.

5. Physical Strength

Includes the properties that determine surface area of the waste form under any given circumstance.

Each of the waste form properties within these five groups of dependent variables is discussed in more detail in Section 8.0.

7.0 EXPERIMENTAL APPROACHES TO WASTE FORM CHARACTERIZATION

Several different experimental approaches are utilized in waste form characterization. The necessity for the different approaches is described in this section.

7.1 Experimental Approaches to Compensate for Nonavailability of Actual Waste

Commercial high-level waste is not being made in the U.S. at the present time. Small quantities can be produced at considerable expense in hot cells and used for the most important experiments, but the preponderance of waste form experimentation must be done using various types of simulated waste.

Nonradioactive Simulated Waste. Nonradioactive isotopes exist for many of the elements present in HLW, thus it is convenient to use chemically-simulated nonradioactive waste in many instances, particularly for laboratory scouting and engineering-scale development experiments. Complete chemical simulation is not practical, however, and the use of some chemical standins in these experiments is necessary, as shown in Table 7.1.

Radioactive Simulated Waste. At the present time all but small (<1 kg of product) radioactive tests must also utilize simulated waste, because of the nonavailability of actual commercial HLW. The technique which was used for the engineering-scale experiments in the Waste Solidification Engineering Prototypes (WSEP) program at PNL was to add large amounts of ^{144}Ce to obtain the radioactive heat generation rate of commercial HLW. Hanford Purex plant first cycle waste was used to provide the entire radioactive waste spectrum, but at concentrations much below those in commercial HLW. The remainder of the nominal waste composition was made up in a manner similar to the nonradioactive simulated waste.

New radioactive engineering-scale experiments may be made at PNL in which the radioactive heat will be obtained from ^{137}Cs (sufficient ^{144}Ce is no longer available at Hanford). It is planned to obtain the fission product and actinide spectrum, at approximately 1% and full level, respectively, from spent power reactor fuel elements.

TABLE 7.1. Representative Chemical Standins Used to Prepare Simulated Nonradioactive High-Level Waste^(a)

<u>Waste Constituent to be Substituted</u>	<u>Reason for Substitution</u>	<u>Substitute Used^(b)</u>
Rb	Expense	K
Y & RE	Expensive to simulate fission product spectrum	Commercially available rare earth mixtures
Tc	No nonradioactive isotope	Mo
Ru	Expense	Fe
Rh	Expense	Co
Pd	Expense	Ni
Cs ^(c)	Expense	K
U, Np, Pu, Am & Cm	No nonradioactive isotopes	Rare earths

- (a) Inexpensive nonradioactive isotopes are available for all of the fission products not shown.
- (b) Substitutes shown are those which have been used in the Waste Fixation Program at PNL.
- (c) Substituted in engineering-scale tests only.

7.2 Experimental Approaches to Study Aging Effects

A fundamental facet of waste form characterization has to be the realization that the time span over which it is desired to be able to predict properties of the waste form is immensely long (see Table 6.1). Methods of experimentally compressing the time frame must be utilized. These are described in Table 7.2 and will be discussed in more detail in Section 8.0. Even with a compressed time frame these experiments can last several years. Only certain carefully selected representative waste form formulations will be taken through these complete experimental regimes.

TABLE 7.2. Experimental Methods for Compressing Time Frame

	Experimental Approach	Important Considerations
<u>Radiation Effects</u> (Total radiation dose received by a waste form at any given time is calculable.)	Increase dose rates to achieve total desired dose in a convenient time. Analogies with metamict minerals may be helpful.	Care must be taken to identify dose rate dependencies, if any.
<u>Thermal Effects</u> (Thermal history of a waste form can be projected by calculation.)	Determine reaction kinetic parameters including temperature coefficients so that extrapolation of rates to low temperatures can be done with confidence.	Kinetics are complicated because of heterogeneous reactions. For example, temperature predictions must consider possibility of thermal conductivity and structural changes.
<u>Leaching and Weathering Reactions</u> (Circumstances by which water could conceivably contact the waste form can be postulated.)	Experimentally simulate the postulated conditions and collect data. Define reaction mechanisms operating at the postulated conditions in order to extrapolate leach behavior to experimentally impractical times. Analogies with the weathering of naturally-occurring minerals and ancient glasses can help corroborate the extrapolations.	Conclusions based on accelerated leach tests made at elevated temperature may not be valid for lower temperature leaching conditions.
<u>Synergistic Effects</u> (The combination of total radiation dose and thermal history can be calculated for a waste form at any projected time.)	Develop understanding of interactions of the effects of radiation and temperature on all properties of the waste form.	The time during history of waste form at which thermal effects are maximum will not coincide with time of maximum radiation effects. Thorough understanding of these interrelationships is required.

7.3 Necessity for Screening Tests

A complicating problem to be faced in carrying out a waste form characterization program is the multitude of potential waste and additive compositions which need to be considered (see Section 6.1.1). Obviously not all can be given an intensive characterization. Thus screening tests serve as a winnowing process for selection of a certain few formulations for detailed characterization. However, flexibility, i.e., the ability to accept some fluctuation in waste composition and processing variations, is an essential ingredient of a successful waste immobilization process. The limits of compositional fluctuations must be defined, in a combination of screening and detailed characterization.

7.4 Effects of Engineering-Scale Operation

The waste forms of ultimate interest are the actual forms that become the routine output of operating facilities. It is vital that waste form characterization is not limited to specimens made individually in the laboratory. The effects of operating conditions, in engineering-scale equipment, may produce waste forms which are significantly different in certain aspects from those made in the laboratory. Thus it is important that, when they are available, waste forms produced in engineering-scale equipment are included in the characterization program.

7.5 Experimental Approaches in Use at Pacific Northwest Laboratories

The several different experimental approaches being used to characterize waste forms at PNL are shown in Table 7.3. Some of the experiments must follow in sequence, but many can be done in parallel in order to facilitate the first waste form characterization (of silicate glass HLW forms) within the time available. The whole characterization process is integrally interwoven with waste form development in an iterative process as shown in Figure 7.1.

The important differences in, and specific uses of, the experimental approaches are outlined in Table 7.3. The details of some of these approaches may vary (those shown are quite specific to PNL facilities), but it is believed that few if any of these general classes of approaches can be omitted from a thorough characterization.

TABLE 7.3. Experimental Approaches to Waste Form Characterization

Approach	Waste				Size of Sample Specimen	Use
	Source	Noble Metals	Beta Gamma	Actinides		
Screening Evaluation	Simulated	No	No	No	40-1,000 g	Glass formulation development, selection of formulations for examination in greater detail.
Laboratory-scale, nonradioactive or tracer level activity	Simulated	Yes	Tracer	Tracer	100-1,000 g	Obtain detailed baseline data for correlation with fully radioactive and engineering-scale waste forms, particular emphasis on long-term thermal effects, phase characterization, and property determinations.
Engineering-scale nonradioactive	Simulated	No	No	No	100-300 kg	Obtain data on effects of processing parameters.
Laboratory-scale radioactive	Power Reactor Fuel	Yes	Yes	Yes	20-1,000 g	Obtain early data on waste forms of fully representative composition, processing steps simulated as closely as possible.
Engineering-scale, radioactive	Simulated	No	Yes	Yes	100-150 kg	Obtain data on effects of processing parameters at approximately representative radioactive dose rates. (Use approximately 1% actual HLW, remainder ^{137}Cs and ^{90}Sr .)
Alpha Accelerated	Simulated	Yes	No	Yes	~10 g	Obtain data on long-term radiation effects. (Use much higher dose rates than present in actual waste forms.)
Demonstration Plant	Power Reactor Fuel	Yes	Yes	Yes	~1,000 kg	Verify waste form characteristics under commercial operating conditions.

FIGURE 7.1. Iterative Relationship Between Development and Characterization Programs

8.0 A PROGRAM FOR INTENSIVE WASTE FORM CHARACTERIZATION

The goal of the program has been stated simply in the Objective (Section 2). It is to understand the characteristics of the solidified waste forms so thoroughly that, when they are put away in engineered storage or ultimate disposal, there will be full confidence that their properties are known, and that any changes or interactions with their environment which may occur later are wholly predictable. Although the goal can be stated simply, implementation will require a large and complex effort over several year's time.

8.1 Elements of the Waste Form Characterization Program

The requirements of the characterization program, i.e., the independent and dependent variables which must be quantified, were discussed in Section 6.0. The experimental approaches, or tools, which are available for accomplishing the quantification were described in Section 7.0. The purpose of the waste form characterization plan is to bring these requirements and tools together in an effective arrangement to assure that the goals of the program are accomplished in a systematic and timely manner. The method by which this is being done is shown in Table 8.1. The components of the program shown in Table 8.1 are specific to the waste form being characterized at PNL, silicate glass cast as a "monolith" in metal canisters, but the overall plan, and the level of effort involved, are representative of what would be required for the intensive characterization of any waste form.

A feature of the program is the division of the properties that must be measured into two types "formulation dependent" and "generic." If all of the dependent variables in the reference matrix (Figure 6.1) had to be measured for all possible waste form compositions, and at several levels of each of the other independent variables, the program would be unmanageably large and contain unnecessary overlap. The program becomes practical and still retains engineering significance however because, as shown in Table 8.1, many of the dependent properties are treated as being generic. That is, within a given waste form type, such as borosilicate glass, the property

TABLE 8.1. Elements of the Waste Form Characterization Program

Program Element		Experimental Technique (a)	Priority (b)	Level of Effort Scientist man years for 10-year program)
Glass Formulation Development		A		5
Formulation Dependent Investigations	Leachability (dynamic system)	A,B,C,D,E,F,G	1	10
	Phase Separation	A,B,C,D,E,F,G	1	
	Devitrification	A,B,C,D,E,F,G	1	
	Density	A,B,C,D,F	2	
	Viscosity	B,C	3	
Generic Investigations	Corrosion of Containment (internal)	A,C,D,E,G	1	55
	Corrosion of Containment (external)	C,E,G	1	
	Leachability (static system)	B,D,F	1	
	Phase Characterization	A,B,C,D,E,F,G	1	
	Volatility	A,B,C,D,E,G	1	
	Radiation Effects	D,E,F,G	1	
	Helium Behavior	D,E,G	2	
	Thermal Conductivity	B,E,G	2	
	Thermal Expansion Coef.	B	3	
	Electrical Conductivity	B	3	
	Frangibility (Mechanical Shock, Thermal Shock and Induced Stress)	B,C,D,E,F,G	3	
	Radiolytic Gas Formation	D,E,F,G	3	
Information Correlation and Dissemination		A,B,C,D,E,F,G		10
Development of Standard Tests		B,C,D,E,F,G		15

(a) A = Screening Evaluation (Formulation Dependent)
 B = Laboratory-Scale Low Activity (Generic)
 C = Engineering-Scale Nonradioactive (Generic)
 D = Laboratory-Scale Radioactive (Generic)
 E = Engineering-Scale Radioactive (Generic)
 F = Accelerated Alpha (Generic)
 G = Demonstration Plant (Generic)

(b) 1 = Highest priority, many measurements, in-depth understanding essential.
 2 = Moderate priority, frequent measurements, but little need for in-depth understanding.
 3 = Low priority, only a few measurements anticipated.

is assumed not to be critically composition dependent. Therefore, if the behavior of the property, as a function of radiation and thermal history, is determined in detail for a few reference compositions the results can then be applied to other compositions with only minor, and easily determined, corrections.

In general the characteristics listed as formulation dependent in Table 8.1 are those that can be rapidly and routinely evaluated in screening tests, thus dependencies can be determined over wide compositional ranges. The division between formulation dependent and generic is somewhat arbitrary. For instance, the presence or absence of macro phase separation or devitrification are routinely recorded for all specimens, but in-depth measurements, which include identification of crystalline species, rates of formation, etc., is only done on certain selected compositions in generic-type investigations.

An important point being made in Table 8.1 is that most of the intensive waste form characterization measurements will be of the generic type, thus it is vital that the most representative compositions possible be used for these experiments.

Priorities have been placed on the importance of the properties scheduled to be measured. As more data is collected the priorities may shift but, as of now, it is believed almost half of the properties listed will remain low priority and not require extensive investigation.

Three tasks, not discussed previously, but which must be an integral part of the characterization program, are also listed in Table 8.1. The first, glass formulation development, provides primary input to the program. It defines the reference glass compositions used in the generic investigations, and mounts a continuous effort to improve waste glass formulations and to develop new glass compositions to accommodate any new waste compositions and/or constituents with which the high-level waste immobilization process may be faced. The other two new tasks assure that the output of the program is available and usable by those who need it. Thus, they include information correlation and dissemination and the development of standard tests (with backup data) which can be adapted by industry and the regulatory agency to assure that the waste forms produced in commercial plants meet required standards.

Tentative estimates of the level of effort required to carry out the various parts of the characterization program are also included in Table 8.1.

8.2 Schedule

The schedule planned for the characterization program is outlined in Figure 8.1. A 10-year program is envisioned. The schedule assumes that an engineering-scale high-level waste immobilization plant will begin operation approximately 5 years into the program. The generic investigations and development of standard tests will be completed well before plant startup, so that their input can be incorporated in a technical manual for the plant. Much of the formulation specific investigations will also be completed at this time, however these investigations will continue at a reduced level and eventually assume a plant assistance function for the operating demonstration plant. The major part of the glass formulation development will be done in 2-3 years, to assure that the optimum glass compositions are included in the intensive characterization program.

The last part of the program will be a verification phase in which the solidified waste products from the operating plant are tested and analyzed to verify that a full-scale plant can routinely produce immobilized waste of the quality predicted by the research and development program. The level of effort required during the verification phase will be much lower than that required during the intensive characterization phase. Thus the maximum level of effort will occur over the first approximately 5 years. The level of effort will then gradually diminish, with quality assurance of the waste forms ultimately becoming part of routine plant operations.

The individual tasks in the waste form characterization program are described in further detail in the remainder of this document.

8.3 Glass Formulation Development

Although the addition of radioisotopes to glass results in some unique problems, many of the specialized techniques of formulation, fabrication, and property measurements used by industrial glass manufacturers are also applicable to HLW glasses. Therefore, the expertise of industrial and

FIGURE 8.1. Schedule of Waste Form Characterization Program

University glass specialists is being enlisted in the radioactive waste glass fixation and characterization programs.

It is of paramount importance that the best glass formulations available are included in the product characterization program. One of the goals of this task is to develop techniques by which industry can contribute candidate glass formulations for cooperative evaluation.

Programs to incorporate radioactive wastes in glasses are underway in several European countries and on a time schedule quite similar to that in the U.S. Many of the problems are mutual; therefore, the European work is being followed closely. Their glass formulations are being compared with those being used in the U.S. program.

Some specific goals of the glass formulation development task include:

- a. Optimize low melting ($<1050^{\circ}\text{C}$) waste glass formulations from the standpoint of:
 1. leach resistance (vitreous and devitrified state)
 2. high waste loading
 3. homogeneity
 4. low corrosion of containment
- b. Determine how much additional leach resistance can be gained by utilizing higher melting formulations.
- c. Develop methods for preventing the separation of water-soluble molybdate second phases in waste glasses while still maintaining a fission product loading of 20-25 wt%.
- d. Determine how much intermediate level waste (ILW) can be mixed with HLW before waste glass properties are affected deleteriously.
- e. Develop glass formulations for wastes containing constituents which may be present in high levels under certain plant operating conditions, such as iron, gadolinium and fluoride.

Glass formulation development has the highest priority. The goals listed above should be completed within about 3 years.

8.4 Formulation Dependent Investigations

In this Section and in Section 8.5 the detailed experimental program will be described in terms of the waste form properties which are being measured.

8.4.1 Leachability (Dynamic System)

One of the prime methods of introduction of radioactive material into the biosphere is through contact with water. Even though intentional contact between glass and water will be avoided, a low leach rate provides a greater margin of safety. Leach rates measured after devitrification and various thermal and radiation treatments of the glass are especially important.

The leach rate studies are designed to define the mechanisms by which the radioactive isotopes contained in the waste glass would be released upon contact with water. To do this adequately the leaching behavior should be divided into two aspects, which can be approximated by experiments in which the leach water is replenished frequently and by experiments in which the leach water is not replenished and the system is allowed to reach equilibrium. In this program plan, the former is identified as "leachability (dynamic system)." The latter is identified as "leachability (static system)" and is discussed in Section 8.5.3.

Leachability (dynamic system) is applicable to short-term leachability of the waste form if exposed in water storage basins or surface waters such as rivers, streams or lakes. The short-term dynamic leach rate is applicable until the waste form is put in ultimate disposal because, until ultimate disposal, any accidental contact of the waste form with water will be followed by immediate retrieval actions and containment will be reinstated before long-term equilibrium behavior become a factor. (See Accident/Recovery, Table 6.1.)

Scope of Task. This task will be carried out in close cooperation with the tasks described in Sections 8.4.2, 8.5.3 and 8.5.5, i.e., the leaching behavior of the waste forms will be defined not only as a function of

specific composition but also as a function of thermal and radiation history. Thus the leach test matrix will include specimens with maximum thermal and radiation-induced changes. Goals of the task include:

- a. Correlate leaching behavior with waste form composition, phase structure and surface morphology.
- b. Correlate waste form composition and leaching behavior with the type of surface film, if any, formed on the waste form. Thus, determine advantages of surface film and compositions required to obtain film.
- c. Determine effects of pH, leachant composition (distilled water, ground water, sea water, brine, etc.), flowrate, and temperature on dynamic leach rate.
- d. Develop standard test procedures for comparison and evaluation of waste forms.

This task will be a major component of the waste form characterization program over the next 10 years. During the first 5 years emphasis will be on laboratory-scale testing. During this phase the leaching mechanisms and factors affecting them will be delineated and standard test procedures will be demonstrated. In the next 5 years emphasis will shift to larger-scale "proof tests" connected with the radioactive engineering-scale waste form specimens produced in the pilot plant and later in the demonstration plant.

8.4.2 Thermal Stability

A first goal in development of any chemical process is that optimum conditions be established to obtain the desired product. In this task, we consider the glass making and glass devitrification processes (the short term product), whose characterization and control are of primary importance to successful immobilization of nuclear wastes. A very strong interrelation with engineering scale activities must be maintained. The objective of this task should be to provide a level of technical understanding which will yield the best possible glass under plant scale conditions.

Because the thermal effects task is really the basis on which all other activities must proceed, it is worthwhile here to briefly outline the glass

route to waste fixation. Although a liquid-fed ceramic melter is one process under development, the prior conversion of fission product wastes to an oxide form will most likely be the method utilized during first generation engineering development. The calcine will be reacted with a suitable borosilicate frit at temperatures ~ 1000 - 1100°C either by direct in-can melting or by a variation of pot melting suitable for final pouring of the product into welded steel canisters. As a result of radioactive self-heating, the large canisters may have a centerline temperature $\sim 800^{\circ}\text{C}$ and wall temperatures $\sim 400^{\circ}\text{C}$. After a few decades, the short-lived isotopes will have decayed to low concentrations and maximum temperatures will be less than 100°C , where it can be assumed that no further changes in phase composition or microstructure will occur.

The thermal effects characterization program is divided into two parts. These two tasks are of fundamental importance and will merit a high level of effort throughout the 10 year program. In combination with the radiation effects studies, those tasks must provide the basis for understanding of the waste forms in sufficient detail, so that all reasoned scientific questions can be answered.

8.4.2.1 Phase Separation

The term phase separation, as used here, describes the inhomogeneities which may exist in the glass as-formed, i.e., it defines the baseline glass existing at the end of the glass-making process, which can then devitrify or undergo other alterations due to subsequent thermal or radiation effects. Phase separation can exist, (1) because the original calcine does not fully dissolve, (2) because of liquid-liquid immiscibility, or (3) because reaction products precipitate. Examples of all three types of phase separation are known in the zinc borosilicate waste glasses presently most thoroughly studied. Examples of waste calcine components which do not dissolve readily in silicate systems are CeO_2 and RuO_2 . (Actinide oxides, such as PuO_2 , may behave similarly although this has not been verified.) Spinel-type crystals are found in the glass, which apparently form and precipitate at the glass-melting temperatures. Currently, a liquid-liquid immiscibility phenomenon,

in which a sodium molybdate salt separates and carries with it cesium and strontium, is considered the most serious phase separation problem. As described in Section 6.3, an immediate goal of the glass formulation development task is to find methods of eliminating molybdate separation, using an essentially empirical approach. The in-depth phase characterization studies carried out under the present task will augment and assist in finding the needed glass formulation corrections. A prime goal will be the development of means to inhibit all undesirable inhomogeneities. The following areas will be examined:

- a. Calcine dissolution rates as a function of prior calcination temperatures (an understanding of calcine crystal chemistry is required).
- b. Establishment of liquid phase separation and compositions (rates).
- c. Establishment of crystalline product formation and rates.
- d. Establishment of "solubility" limits below which (b) and (c) do not occur.
- e. Modification of glass formulation to control phase separation behavior.

The experimental approach should rely on microstructural studies (including microprobe analysis) in combination with x-ray diffraction methods.

8.4.2.2 Devitrification

At the storage temperatures experienced after fabrication, a large fraction of the waste glass may become devitrified. The initial centerline temperature can be near optimum for rapid devitrification.

Under normal handling the wall temperature of the waste canisters should not exceed about 400°C. Devitrification occurs very slowly, if at all, at these temperatures. One of the goals of this task will be to measure the rate of devitrification at lower temperatures in order to determine how much devitrification may be expected in the waste glasses as a function of distance out from the centerline of the canister. The main goal, however, is to determine the effect of devitrification when it does occur. The composition and morphology of the crystalline species will be determined, as well as the composition of the residual glass phase, and correlated with effects on:

- leach rate
- mechanical properties
- density (porosity)
- thermal expansion

Of particular importance is the location of the actinides after devitrification. Although the radiation damage problem is discussed in that sub-task, the question of where the actinides will be located (in low molar concentration), i.e., in the glass matrix or as crystalline products, or both, will be very dependent on behavior of the nonactinide species. Thus, the general devitrification process will play a very direct role in subsequent susceptibility of the waste glass to alpha damage and must be fully understood in that respect. Since a well engineered glass-ceramic has some potential advantages over a vitreous glass form, studies should also be conducted to determine the viability of producing this type of waste form.

Goals of the task include:

- a. Determine devitrification products (under wide range of time and temperature conditions) for a variety of waste glass formations to determine trends due to the effects of major compositional variables such as Si, B, Na, Zn, Pb and fission products.
- b. Establish kinetics for the development of the individual crystalline phases.
- c. Identify devitrification species or conditions which should be avoided because of adverse effects on leach rate, microcracking, or other properties.
- d. Determine viability of glass-ceramic waste forms.

8.4.3 Density

Characterization of waste form density yields data useful for a variety of purposes, since density is affected by thermal history, radiation dose, porosity or bubble content, and crystal content.

8.4.4 Viscosity

The viscosity of the waste glass plays a vital role in the solidification process of the resultant product. The rate of homogenization during melting, melter capacity, efficiency, and pouring rates in canister loading,

all depend directly on the viscosity, especially upon its temperature dependence. Thus it is necessary to understand the viscosity of the molten waste glass and the influence of temperature and glass composition on this property.

8.5 Generic Investigations

In the generic investigations, a class (genus) of waste form is assumed to behave in a relatively similar manner, so that a detailed definition of the behavior of one characteristic formulation within the class can be extrapolated to other formulations within the class. By isolating the generic investigations from concern about transitory fluctuations in the formulation of wastes and waste forms it is possible to conduct long-term investigations to develop an understanding of the basic mechanisms governing properties of the waste form. Thus, if a thorough understanding of the properties of a reference silicate glass containing a standard amount of a reference HLW, for instance, is obtained, then as new silicate glass formulations are considered a much less exhaustive investigation will be required to verify an overall behavior pattern.

The generic program elements described in the sections to follow can each be carried out as a relatively independent investigation. The main requirement is that the formulation of the reference waste form be carefully chosen to be representative of a given class of waste form. The composition of the reference waste glass formulation which has been used in the generic investigations at PNL to date is shown in Table 8.2.

8.5.1 Corrosion of Containment (Internal)

In the current solidified HLW handling philosophy, the containment canister is considered the critical line of defense until the waste is finally interred. Thus, the integrity of the canister is of primary importance.

The results of corrosive attack on the canister could be thinning of the walls, loss of strength due to embrittlement and reduced ductility, and general stress corrosion effects. Stress corrosion is believed to be

Composition, Weight Per Cent

the most serious problem. The currently-used austenitic stainless steel canisters are in a highly stressed condition during storage because the coefficient of expansion of the glass cast in the canister is much lower than that of the stainless steel.

8.13

- a. Evaluation of the corrosion kinetics of canister materials such as 300 series stainless steel and Inconel in contact with waste glass as a function of time and temperature. (Times and temperatures must encompass those shown for processing, storage and transport conditions in Table 6.1.)
- b. Evaluation of an expendable, thin walled container for the high temperature portion of pouring or forming the glass in the canister to eliminate sensitizing the outer permanent canister and hence reducing the corrosion rate and induced stress.
- c. Develop a standard test for accelerated evaluation of the interaction between a waste containing glass and a canister under anticipated storage conditions.

In all cases, the studies will have to take into consideration the composition of the glass, any devitrification of the glass, tendencies for phase separation in the glass, and pressurization of the canister due to outgassing and helium generation.

Up until now in this section an in-can melting process has been assumed. Active consideration is also being given processes using a separate continuous melter which may be constructed of either a high temperature resistant metal, such as Inconel, or a ceramic, as in conventional glass furnaces. Corrosion measurements for these conditions are also included in this task.

8.5.2 Corrosion of Containment (External)

Canister interactions with the environment, which act in any way to reduce the integrity of the canister before the waste is placed in the ultimate disposal site, must be minimized. Therefore, (1) the canister must be fabricated from a material which is inherently corrosion resistant in air and water storage basins and (2) the processing and handling steps must be designed to maintain the full corrosion resistance potential of the canister.

The canisters can be fabricated from very well characterized materials, such as the 300 series stainless steels which have been used most extensively to date in development studies producing calcine or glass waste forms. Even though the canister materials may be well characterized, additional characterization is required to define the special effects which processing and handling may have. Possibly the largest unknowns are associated with the possible stressing and sensitization of the canister wall which may occur. These are functions of canister design and processing parameters and can best be studied on an engineering-scale, as shown in Table 8.1. Characterization of the filled canisters, including weld closures, must be an integral part of the engineering and demonstration plant programs. Therefore the radioactive engineering-scale program will include storage of the canisters under prototypical water basin and RSSF conditions. The canister walls will be tested periodically, both nondestructively and destructively (via trepanned samples).

Priority should be given two interrelated studies:

Stress Reduction. The canister walls can be highly stressed, if filled with a hot waste form which has a thermal expansion coefficient different from that of the canister material. For instance, stainless steel canisters filled with silicate waste glass are stressed beyond the yield point of the steel when they cool. Stress reduction methods should be sought. These can include changes in canister design, such as crushable or sacrificial liners, or selection of new canister materials and/or waste form formulations with more closely matching thermal expansion coefficients.

Code Requirements and Double Encapsulation (Overpacking). The possibility exists that the filled waste canisters may not meet the nuclear processing vessel code requirements, although this has not been determined. In this event each canister will possibly have to be overpacked with a code vessel. The characterization program is impacted directly because the waste form "package" must be characterized now becomes the initial filled waste canister plus its overpack.

These two studies should be completed as soon as possible so that the engineering-scale radioactive studies, which will start at PNL in 1976, can incorporate their findings.

8.5.3 Leachability (Static System)

Behavior in a static system can be used to describe the long-term dissolution characteristics of the waste form in a geologic environment, in particular, the ultimate disposal environment, but it will also apply to the nonretrievable debris from an accident (see Table 6.1). Whereas the initial leach rate may be considered, as a first approximation, to be an incongruent diffusion-controlled phenomenon, as dissolution continues the process is usually considered to become more congruent with the surface "dissolving" uniformly. Determination of the release of a specific isotope is made more complicated due to the possible formation of new precipitates at the surface, and ion exchange reactions with neighboring material. The first-order dissolution and precipitation rates, Equations (1) and (2) below, have been shown to apply to dissolution of a number of silicate minerals on a geologic time scale in aqueous solutions,^(8,9,10) and should also be applicable to silicate waste forms in ultimate disposal sites.

$$\text{Rate of dissolution} = b_1 (C_{1,s} - C), \quad (1)$$

$$\text{Rate of precipitation} = b_2 (C - C_{2,s}), \quad (2)$$

where rate is expressed in mass per unit volume of pore water per unit time, b is a rate constant (time^{-1}), C is the concentration in solution, C_s is the concentration at saturation, and subscripts 1 and 2 refer to the dissolving and precipitating mineral phases, respectively.

No information is currently available on the saturation or equilibrium behavior of waste forms. These data are needed to predict long-term waste form stability in ultimate disposal.

Scope of Task. This task will be carried out in close cooperation with the tasks described in Sections 8.4.2 and 8.5.5, i.e., the leaching

behavior of the waste forms will be defined not only as a function of specific composition but also as a function of thermal and radiation history. Thus the leach test matrix will include specimens with maximum thermal and radiation-induced changes. Goals of the task include:

- a. Determine saturation concentrations for waste forms in site-specific geologic disposal situations.
- b. Perform soil column percolation tests with fully radioactive waste form specimens.
- c. Perform large-scale burial tests of fully radioactive waste form specimens.

This task will be a major component of the waste form characterization program over the next 10 years. During the first 5 years emphasis will be on laboratory-scale testing. During this phase the leaching mechanisms and factors affecting them will be delineated and standard test procedures will be demonstrated. In the next 5 years emphasis will shift to "proof tests." During this period carefully monitored environmental burial tests will be started to further verify the soil column and other laboratory measurements.

8.5.4 Volatility

Vaporization of some constituents from fission product-containing waste forms can occur during processing, or in possible accident situations during shipment or storage. Recent studies on wastes incorporated into a zinc borosilicate glass (the initial generic waste glass being characterized at PNL) have shown the most volatile element to be Cs, but that smaller amounts of Rb, Mo, Ru, and Te, as well as B, Na, and K from the glass frit, are also vaporized. The greatest potential improvement to the waste form, from a volatility standpoint, would be to reduce the Cs volatility if this can be done without degradation of other properties. During processing, on the other hand, Ru is the most volatile component and processing problems would be reduced if the Ru volatility could be lowered.

As shown in Table 8.1, a wide range of experimental techniques should be employed in volatility studies. Volatility during processing can best

be measured in prototypical engineering-scale equipment; it is often difficult to simulate processing conditions in the laboratory. Identification of all of the troublesome radioactive species can best be obtained in tests with full-level waste. Laboratory-scale tests with simulated waste compositions can be used to measure the effects of such parameters as temperature and atmosphere on the release rate of specific species.

The release rate is likely to be diffusion-controlled. For best understanding of the release process the diffusion coefficients should be determined. Better quantitative data and extension of data to lower temperatures can be obtained by spiking the waste forms with radioactive isotopes to increase analytical sensitivity.

The definitive characterization of volatility from a generic waste form should include:

- Identification of the volatile elements and molecular species, both radioactive and nonradioactive.
- Determination of the release rates of the volatiles during processing.
- Determination of the release rates from the waste form during possible accident situations.

8.5.5 Radiation Damage

Fission product containing wastes are subjected to potential radiation damage from alpha, beta, gamma, neutron, and fission fragment sources. Alpha decay of the actinides is expected to be the major contributor with each ~ 5 MeV event creating thousands of displacements and broken chemical bonds (in covalent materials). In addition, the considerable quantities of helium generated must either diffuse out of the solid or be otherwise accommodated without producing internal stresses leading to fragmentation. It must be assumed at this point that significant volume changes will occur, especially in a devitrified glass, or other crystalline waste forms as damage accumulates.

During the first years of storage, self heating will tend to anneal out the effects of radiation. After a few decades, however, the waste will

be at ambient temperatures and high concentrations of long half-life actinide isotopes ensure that significant radiation will be present for millions of years. Geologic evidence from actinide bearing minerals suggests that all silica base systems approach the glassy "metamict" state as a result of this long-term radiation, but physical integrity is maintained. In high level waste glasses, however, the radiation dose rate will be many orders of magnitude higher than occurs in natural minerals. To place our present state of knowledge in proper perspective in this area, it is perhaps useful to remember that the nuclear industry is now 30 years experienced and we need to ensure the stability of a radioactive waste for many thousands of years. While this is a formidable task, it can be countered that short-lived actinide isotopes ($^{238}\text{PuO}_2$, $^{224}\text{Cm}_2\text{O}_3$) have been prepared in pure form as high density pellets for heat source applications. These materials have been the subject of many years research and although affected by radiation damage, do not grossly deteriorate, although the dose rate is $\sim 10^{21}$ α -events/cm³-yr ($^{244}\text{Cm}_2\text{O}_3$). For nuclear fuel wastes, the cumulative dose is expected to be about 2×10^{18} α -events/cm³ for the first 100 years and 5×10^{19} α -events/cm³ after 10^6 years.

The general acceptance of silica base waste forms stems from the need to immobilize a large fraction of the periodic table in a single matrix with simplicity, and in a form compatible with and similar to known geologic systems. A silicate formulation is thus a favored form, but is one of the least favorable, with respect to radiation damage. Although excellent stability has been indicated above for cubic fluorite related oxides, the low crystal symmetry and strong covalent bonds in silicate compounds lead to a strong dependence of all properties on radiation damage level.

Characterization of radiation effects in crystalline waste forms, and devitrified glasses, is complicated by the fact that the actinides may be highly concentrated as microcrystals, with crystal chemistry dependent on valence (Cm^{3+} , $\text{Am}^{3+,4+}$, $\text{Pu}^{4+,6+}$, U^{6+}). In actual wastes, the concentrations of the major alpha emitters will be <0.2 wt%, so that doping studies at much higher concentrations must be undertaken with care. It is necessary that microstructural studies be made to locate all actinide containing phases;

that high level doping studies be undertaken with recognition of this possible damage concentration effect; and that alpha particle and other heavy ion bombardment be utilized to achieve an understanding at the highest damage levels attainable.

The purpose of the radiation damage studies is to understand all effects of radiation damage on the candidate nuclear waste form to a degree that its integrity can be projected to endure over the first 10^6 years of storage. A program of study is outlined in Figure 8.2 in which accelerated irradiations are achieved through ion bombardment (including use of actinides as external alpha sources) and through actinide doping. It will be important to examine both vitreous and devitrified samples (of various microstructures) and to establish the kinetics of radiation damage ingrowth and damage annealing behavior. The correlation of microstructure to effects on the properties indicated should provide the necessary level of understanding. In addition, the effects of radiation on microstructural alterations such as bubble formation, incipient crack formation, etc. will be defined.

8.5.6 Helium Diffusion

Helium will be produced in the waste form from alpha decay at a rate controlled by the actinide concentrations. It is possible that helium pressurization of the waste canisters could occur, if the waste contains sufficient actinides and if the helium is not held within the waste form. Secondly, if the actinides are locally concentrated, the helium generated will be correspondingly concentrated producing high localized stresses and possible cracking. Therefore it is important that helium solubility and diffusion coefficients be determined in the waste form and that the dependence on radiation damage be examined. In some instances it may be necessary to require that a certain void volume be reserved in the waste canister to accommodate the accumulation of released helium.

8.5.7 Thermal Conductivity

Thermal conductivity of the solid waste is a major factor which determines the maximum temperature and temperature profile of any particular

FIGURE 8.2 Characterization of Radiation Effects on Waste Glass

waste form. The maximum temperature will be influenced by the radioactive element concentration and the geometry of the canister. Storage temperatures will influence the waste product performance and other properties during storage, e.g., annealing, devitrification, fracture, etc. The thermal conductivity and thermal diffusivity of the molten waste glass is important to the melting process including the melter design and operation, namely, efficiency, heating and cooling rates, and the design of the canister. Thus a knowledge of the thermal conductivity/diffusivity of all waste forms, and of molten waste glass in particular, are critical to the development of optimum waste solidification processes.

8.5.8 Thermal Expansion Coefficient

Thermal expansion will directly influence the waste solidification process. Mechanical compatibility of the waste form with the container and the potential for fracture under a thermal gradient are important aspects of thermal expansion mismatch between the canister and the solid waste. For a molten glass product, the solidification behavior, fracture behavior, and heating and cooling cycles require a knowledge of the thermal expansion. In addition, thermal expansion data are valuable tools which can be used to identify other important characteristics of solidified waste such as annealing behavior, softening points, and devitrification phenomenon.

8.5.9 Electrical Conductivity

Electrical conductivity of molten waste glass is of major concern in the direct joule heating of waste glasses in a ceramic lined glass melter. The design of the electrodes and electrical power supply, preheaters, and general operation can be performed with more efficiency if electrical conductivity of both the solid and molten waste glass are known as a function of temperature and waste composition. Thus, knowledge of the electrical conductivity can be used to improve the waste product.

8.5.10 Frangibility (Induced Stresses and Mechanical and Thermal Shock Resistance)

The toughness of any waste-containing brittle solid is a matter of concern. During processing, toughness will influence, directly or indirectly, the amount of thermal stress cracking which occurs. During transport and storage, toughness implies a degree of impact damage resistance. Once the waste is placed in geologic storage, impact is no longer relevant, but stress buildup from long-term thermal and/or radiation effects may also require a high degree of toughness. Although any reference glass waste form is fundamentally brittle, some latitude exists as to the degree of brittleness. For instance, devitrified glasses are generally tougher than those in the glassy state, and usually have a lower expansion coefficient, producing higher thermal shock resistance. Toughness influences the leach resistance required of a given waste form directly, since it influences the area exposed for possible leaching.

The rather large canister size required, based on reasonable production capacities and processing parameters, almost certainly dictates that a glass waste form will not be produced crack-free. The extent of thermal shock cracking, and thus the size of the fragments produced is determined by the properties of the glass and the cooling cycle. A small amount of acoustic emission testing has been performed which provided information on when cracking of the PNL reference glass waste form occurred during cooling. This technique should be investigated further, as cooling cycles could be designed more knowledgeably if the information thus available were combined with calculations of expected stress levels. For glass waste forms, it might even be desirable to introduce a few stress raisers to help crack the glass controllably into pieces of a reasonable size during cooling.

The information gained from previous acoustic emission testing showed that cracking did not take place at high temperatures. It is possible that glass could be devitrified via a controlled cooling cycles and in this way produce the desired monolith. Because of the heat generated by the waste,

the concept above refers only to the outer radial sections of the canister. The core will probably devitrify whatever the thermal treatment.

During generic investigations of the frangibility of candidate waste forms the fracture energy will be determined by a simple technique so that differences in toughness can be quantified. The work-of-fracture technique is one in which the work necessary to propagate a crack across unit surface area is measured. The results thus obtained will comprise good base line data for comparison with other waste forms. Conventional impact testing and product analysis to physically define the degree of glass breakup will continue.

The effect of radiation damage on toughness will also be determined. Using accelerated alpha effects techniques, samples doped with an appropriate alpha-emitter and self-damaged will be obtained and tested for work-of-fracture to note any changes occurring as a result of stresses resulting from radiation damage.

8.5.11 Radiolytic Gas Formation

The conditions under which radiolytically-formed gases could potentially form in concentrations sufficient to pressurize the canister should be defined for each generic waste form so that these conditions are avoided. Among the radiolytic gases of concern are O_2 , H_2 , CO_2 , N_2 and various oxides of nitrogen. Their precursors, nitrate salts, bound water, degraded organics, etc., are all thermally unstable and can be removed to innocuous levels if, during processing, the waste form receives a sufficient heat treatment.

Normal waste calciner operating temperatures are not high enough to assure thermal decomposition of the gas forming precursors, but the viable candidate HLW immobilization processes involve a subsequent higher temperature processing step to insure that the gas-forming precursors are indeed eliminated. The goal of the radiolytic gas formation investigation is simply to verify that the gas-forming precursors are removed to harmless levels. As shown in Table 8.1, this will be done in a combination of

experiments utilizing, (1) accelerated alpha techniques to simulate long-term storage (where gases may buildup which would not at shorter times because of gamma radiation-catalyzed recombination), and (2) engineering-scale specimens to verify that the process actually achieves the removal of the gas-forming precursors as designed. The latter experiments will involve measuring the pressure in sealed waste canisters and also analyzing the gas phase within the canister periodically.

8.6 Information Correlation and Dissemination

Currently most of the waste form characterization data being obtained in the U.S. is reported incrementally in bimonthly or quarterly reports from the various ERDA laboratories, some of which receive only limited distribution. This method of information dissemination would be augmented very beneficially by the publication of periodic topical reports, in which the data available on the properties of a specific waste form(s) are correlated in detail. Such detailed reporting is a basic aspect of the comprehensive waste form characterization program described in this document.

It is planned to publish annual status reports on the progress in the intensive characterization of silicate glasses for the immobilization of high-level waste at PNL, beginning in October 1976. These reports will correlate the properties of glasses of varying composition with thermal and radiation history in a systematic manner. They will include in depth descriptions of the progress on the generic investigations made on silicate glass waste forms.

8.7 Development of Standard Tests

A continuing problem in the development of radioactive waste forms is the definition of what properties the waste form must have. The current regulations give guidelines, i.e., the waste form must be a "dry solid" which is "chemically, thermally and radiolytically stable." Practical implementation of these guidelines, and any other criteria which may be imposed on the waste forms, requires that a list of specific tests be developed.

It is important that the standard tests be developed as soon as possible so that a backlog of experience with their use can be accumulated at ERDA laboratories. This will permit their application for enforcing regulations to be evaluated before the time that enforcement of regulations at commercial plants is required.

It is envisioned that the standard tests will be generally applicable ASTM-type tests, which are designed for routine use and which do not require sophisticated equipment. They can be proof-type tests, and in most cases probably won't be the same tests that are used for the fundamental waste form characterization described in the earlier sections of this document.

Standard tests for the following properties of the waste form are needed:

- Chemical Stability { Leachability
Canister Interactions
- Gas Content
- Thermal Stability
- Radiation Stability

Tentative tests for these properties should be established by early 1976 for initial evaluation. The need for standard tests for other properties may also become apparent as waste form development continues.

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