Annual Report on the Development and Characterization of Solidified Forms for High-Level Wastes: 1978

**W. A. Ross
J. E. Mendel**

December 1979

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Pacific Northwest Laboratory
Richland, Washington 99352

SUMMARY

J. E. Mendel

Development and characterization of solidified high-level waste forms--a major program at the Pacific Northwest Laboratory (PNL) for several years--is continuing. These efforts are directed at determining both process properties and long-term behaviors of various solidified high-level waste forms in aqueous, thermal, and radiation environments. Glass waste forms for defense wastes were emphasized in 1978, and investigations of the long-term behavior of power-reactor waste glasses were continued. The characterization of alternative waste forms, including crystalline forms, coated particles and metal matrices, is being done by the same techniques that are being used for waste glasses.

Waste form specifications are not yet defined. The goal of waste form characterization is to measure the important properties and potential reactions of candidate waste forms. Judgments on the acceptability of the values obtained in measurements on the different candidate waste forms will come from analyses of the total multibarrier waste management system. Such an analysis is included as the Appendix, which compares the leaching behavior of waste forms with the known behavior of natural ores. The results to date indicate that the isolation achieved in a geologic repository is relatively insensitive to leach rate over a wide range.

A new and promising computer-based approach to waste glass development was initiated at PNL this year. The objective is to develop a model of glass properties over broad compositional ranges so that, given a particular waste for vitrification, the most promising compositional field can be immediately identified. Two studies exploring the new technique were completed and a third was started. The waste glass properties that were measured as a function of composition were melt viscosity, melt electrical conductivity, devitrification, and chemical durability. The alkali metals were found to have the greatest effect upon glass properties. When expressed as a function of mole-percent, no difference could be found in the effects of sodium, potassium and lithium. Titanium caused a slight decrease in viscosity and a significant increase in chemical durability in acidic solutions (pH-4). Aluminum, nickel and iron were all found to increase the formation of nickel-ferrite spinel crystals in the glass.

The development of glass waste forms is nearing completion, although characterization of long-term behaviors continues. Laboratory development and characterization of alternative or advanced waste forms that can potentially offer further incremental improvements in safety are receiving increased emphasis. Four multibarrier advanced waste forms were produced on a one-liter scale with simulated waste and were then characterized. Glass marbles encapsulated in a vacuum-cast lead alloy provided improved inertness with a minimal increase in technological complexity. Supercalcine spheres exhibited excellent inertness when coated with pyrolytic carbon and alumina and put in a metal matrix, but the processing requirements are quite complex.

Canister development efforts emphasized confirmation of computer codes by means of experimental data. The computer codes predict stress in the canister wall and in the contained glass. Heat transfer codes applied to canisters of waste glass also correlated well with empirical data.

During 1978 the scope of the leaching studies at PNL continued to broaden. We are now attempting to not only define initial leach rates for various waste forms in realistic environments, but also to project what they are likely to be well beyond experimentally verifiable times. We are also attempting to define what a given leach rate means in terms of geologic isolation.

The results of tests on simulated and actual high-level waste glasses continue to suggest that thermal devitrification has a relatively small effect upon mechanical and chemical durabilities. Although the identity of the individual crystalline phases appearing upon devitrification of waste glasses is highly dependent upon the glass composition, there is a general similarity in devitrification kinetics because all the waste glasses have been formulated to have a viscosity of less than 200 poise at 1050°C. Formation of large crystals has been observed to cause microcracking, but this can be avoided in all of the glasses by maintaining storage temperatures at below 650°C.

Tests on the effects radiation has upon waste forms also continue to show changes to be relatively insignificant. The effects caused by decay of actinides can be estimated to saturate at near 10^{19} alpha-events/cm³ in homogeneous solids. Actually, in solidified waste forms the effects are usually observed to saturate in the range 2 to 5 x 10¹⁸ alpha-events/cm³. Microcracking has been observed around certain crystals as radiation causes amorphization and swelling of the crystals. However, no deleterious macro-effects on the waste forms containing the crystals have been observed.

A significant portion of the characterization measurements are now being made on glass containing simulated nonradioactive waste that is made in engineering-scale equipment. Certain homogeneity problems will be difficult to detect until fully radioactive runs are made. In particular, insolubles such as CeO₂ or spinel crystals can form viscous sludges in the bottom of continuous glass melters. Samples of such sludges were characterized; formulations for their elimination are being developed.

As other waste forms are developed to the point that they can be produced in engineering-scale equipment, characterization of those products will also become an important part of the program.

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I. INTRODUCTION

W. A. Ross

In conjunction with the Department of Energy (DOE), the Pacific Northwest Laboratory (PNL), operated by Battelle Memorial Institute, continues to develop technology for solidification and disposal of high-level radioactive wastes (HLW). This is the third annual report prepared to summarize PNL research and development activities on waste forms.

The first and second annual reports (Mendel et al. 1977, Ross et al. 1978) were prepared as a result of the Program Plan for the Comprehensive Characterization of Solidified High-Level Wastes issued in late 1975 (Mendel et al. 1975). These first two reports were focused primarily upon the characterization of commercial waste glasses; data from them and from this report have been compiled in a comprehensive report (Mendel 1978).

This year's annual report has been expanded to include all waste materials, including defense waste glasses, spent fuel, and alternative waste forms--in addition to HLW glasses; the report includes developmental as well as characterization results. The annual's primary source of information is the High-Level Waste Immobilization Program (HLWIP). In addition to laboratory-scale waste form development and characterization, the HLWIP includes engineering-scale development (on both a nonradioactive and radioactive basis) of processes for producing solidified radioactive waste forms. Progress in the HLWIP is reported in quarterly reports. The most recent report, which includes a listing of all previous reports, is PNL-3050-2 (McElroy et al. 1979e).

A large amount of leaching work on waste forms in geologic environments is being done at PNL in a related program--the Waste Isolation Safety Assessment Program (WISAP)--which is sponsored by DOE's Office of Nuclear Waste Isolation (ONWI). Since the leaching work in the HLWIP is coordinated closely with that in the WISAP, the latter leaching program is also described briefly in this report. Progress in the WISAP is also reported quarterly, with the most recent report being PNL-2885-3 (Brandstetter et al. 1979).

Detailed evaluations have continued to emphasize materials development, leaching behavior, thermal effects, radiation effects, mechanical comparisons, and application to full-scale systems. With the expanded scope of this report and the desire to keep it of readable size (and therefore usable), we have attempted to summarize as much as possible. References are supplied to assist in the location of additional information. Also, each section's authors and contributors are noted accordingly.

II. WASTE COMPOSITIONS

J. L. Swanson

Flowsheets are being developed for the final disposal of the defense HLW currently stored in neutralized form at Savannah River and Hanford. Since the volume of these wastes is very large and since the activity (except for ^{137}Cs) is concentrated in the sludge that formed after neutralization, the plan is to separate the radioactive sludge from the supernate before proceeding with immobilization. This will greatly reduce the volume of radioactive waste that must be immobilized. The supernate can be treated as an extremely low-level waste after the ^{137}Cs , residual ^{90}Sr and plutonium ions are removed. These materials are then combined with the washed sludge for immobilization. Final selection of the waste form for immobilization of the defense wastes at Savannah River is scheduled for about 1982.

The waste form that is selected will have to be adaptable enough to accommodate a wide variety of waste compositions. As shown in Table II.1., the sludge from each waste tank has a different composition, though iron and aluminum are always major constituents.

Commercial waste compositions were detailed in last year's annual report, which also contained the glass code explanation (Ross et al. 1978).

TABLE II.1. Analysis of Washed Waste Sludges
at Savannah River (a)

Metal Ion	Sample Composition, wt%									
	4, 6	5	5	7	12	13	13	15	15	16
Fe	33.0	29.0	28.0	8.9	4.5	26.0	28.0	5.3	3.1	14.0
Al	2.3	1.6	1.5	2.5	30.0	8.7	7.1	19.0	34.0	17.0
Mn	2.0	5.8	11.0	2.2	1.7	7.8	8.8	2.4	2.3	2.6
U	9.2	11.0	15.0	3.3	(b)	4.2	4.0	3.8	0.9	4.5
Na	3.0	5.7	6.1	2.8	1.0	2.6	3.1	2.4	1.2	2.2
Ca	2.3	0.9	0.6	0.8	2.1	1.8	2.3	0.5	0.2	2.9
Hg	0.6	0.1	0.1	0.06	1.1	2.3	2.1	2.5	0.9	2.8
Ni	6.3	6.3	5.1	2.1	0.5	0.4	0.5	0.7	0.5	0.3
C	--			17.0						
Si	--			3.2						
Bi	--									
<u>Anions</u>										
NO_3	0.1	1.2	3.0	1.2	0.4	0.3	0.5	0.2	5.0	0.3
SO_4	0.5	0.5			0.5	0.5		0.5		0.5
Cl^-				2.0			1.0			

(a) Ref. DP-1399 and DP-1441

(b) No data

III. WASTE FORM SPECIFICATIONS

J. E. Mendel

The goal of the HLWIP is to immobilize high-level radioactive wastes in the form of stable, inert solids. Detailed specifications for the properties that the solidified waste forms must possess to qualify as being "stable" and "inert" have not yet fully evolved. The Nuclear Regulatory Commission (NRC) is expected to provide guidance in this area late in 1979.

The solidified waste form is an integral part of much of the waste management system, including: 1) waste immobilization processing, 2) interim surface storage, 3) transportation, and 4) deep geologic disposal. The requirements of deep geologic isolation are dominant for two major reasons. First, most of the lifetime of the waste forms will be spent in geologic disposal, where both surveillance and remedial action are difficult. Second, waste form requirements may differ depending upon the type of rock in which the geologic repository is located--i.e., certain waste form specifications could be site-specific. Although deep geologic isolation demands much attention, the other parts of the system also place significant requirements upon the properties of the waste form and must also be given their due consideration.

THE ENGINEERED BARRIER SYSTEM

The deep geologic disposal system utilizes a system of multiple barriers to obtain the highest assurance of reliability. The stable, inert solidified waste form is only one component of the system. All of the components of the system are shown in Figure III.1. A feature of the engineered barrier system is the possibility of adding barriers. For a given repository, fewer or more barriers than those shown here may be used. Briefly, the functions of the engineered barrier system components are as follows:

- Overburden - A repository depth of 600 m or more assures that any water which might possibly be contaminated by repository contact will have such a lengthy, time-consuming path to travel before reaching the biosphere that the radionuclides will either be adsorbed on the soil or will decay to harmless levels.
- Near-Field Geology - The repository will be located within a deep geologic formation specially selected for its dryness and impermeability.
- Specially Designed Engineered Barriers (optional) - Additional engineered barriers can be incorporated into the repository design for special purposes. For example, materials that will swell when contacted with water may be used to prevent water from reaching the solidified waste forms, and materials that will adsorb radionuclides from water (should leaching occur) may also be included.
- Overpack (optional) - Another type of engineered barrier--the overpack is usually considered to be a secondary canister. The overpack can be designed to be an absolute barrier for finite periods in the repository. For instance, design lifetimes of 500 yr are feasible and would permit the ^{90}Sr and ^{137}Cs in the waste to decay to harmless levels.

FIGURE III.1. Engineered Barrier Concept for Waste Isolation

- Canister - The sealed metal canister holding the solidified waste constitutes the primary barrier to dispersion of the radioactivity in the waste during handling, interim surface storage and transportation of the waste, but canister lifetime may be limited after the waste is placed in a geologic repository.
- Solidified Waste Form - The function of the solidified waste form is to immobilize the high-level liquid waste in a stable, inert form that is compatible with the storage canister and with deep geologic disposal.

The barriers can be divided into two main types: absolute and rate-limiting. The first is exemplified by the canister, by many of the engineered barriers, and by some near-field geologic formations; the second is represented by the overburden, the solidified waste form, and some engineered barriers. In analyses of long-term behavior, the absolute barriers are step functions: at the end of a finite life their contribution becomes negligible. The rate-limiting barriers then take over to further suppress the movement of the residual radioactivity.

WORKING-HYPOTHESIS WASTE FORM SPECIFICATIONS

During this interim period, while waste form specifications are being defined, certain working hypotheses are being used. Among these are:

- Solidified HLW will be disposed of in deep geologic repositories; thus, the expected long-term behavior of the solidified wastes in the repositories must be defined.
- Repository design may dictate certain waste form requirements; however, the waste form must still remain compatible with processing, interim storage and transportation.
- Geologic repositories will utilize an engineered barrier system.

Most solidified waste forms behave as rate-limiting barriers to the release of radioactivity. Thus, specifications applied to the waste forms ideally should define the degree of suppression that must be achieved in representative situations--especially in geologic repositories. The properties of the waste form should be predictable at any time in the repository. The major purposes of waste form characterization then become: 1) demonstration of waste form compatibility with absolute containment during its early history; 2) determination of what, if any, long-term effects temperature and radiation may have upon the waste form; and 3) determination of how the waste form will behave in situations (including accidents) in which it may be exposed to the surroundings. Judgments on the acceptability of candidate waste form behavior will come from analyses of the total multibarrier system.

IV. WASTE FORM DEVELOPMENT: GLASS

L. A. Chick, G. B. Mellinger

A number of properties are important when evaluating potential waste glass compositions. Among these are viscosity, electrical conductivity, and solids in the molten glass at processing temperatures. Others, which are important in the final product, are chemical durability and devitrification resistance. The behavior of each different glass is dependent upon its composition.

To date, most waste glass development has proceeded in an iterative manner: a proposed glass was tested, the developer decided which properties needed improvement, and adjustments to the composition were proposed to yield more acceptable properties. The new compositions were then tested and the process was repeated.

This year we have established a new approach to waste glass development at PNL. The objective is to develop an understanding of glass properties over broad compositional ranges so that, given a particular waste for vitrification, we will know better where to begin looking in the compositional field and will consequently find the optimal composition more efficiently.

Two studies exploring the new technique have been completed; a third is under way. Here we report the highlights of these studies and discuss a more comprehensive study to be begun in the coming year.

ONE-AT-A-TIME VARIATION STUDY ON DEFENSE WASTE GLASSES

Procedure

In this study the effects that fifteen oxide glass components have upon glass properties were studied by establishing a base glass composition and changing the concentration of one component at a time while holding the other components at their base-glass proportions. The range of component variation is shown in Table IV.1. The base glass composition shown was a glass being considered for possible vitrification of a defense waste containing high levels of Al_2O_3 , Fe_2O_3 and MnO_2 .

Viscosity and electrical conductivity were measured at 1070°C . The crystallinity present in air-quenched samples was determined from photomicrographs. Chemical durability was tested in buffered pH-4 and pH-9 solutions at room temperature for 19 hours. A third sample was subjected to a Soxhlet (99°C distilled water for 24 h). In each case, sample weight loss was measured.

Results

Table IV.1 summarizes the results. The alkali metals (Li, Na, K) were found to have large effects upon nearly all properties measured. When property data were plotted as a function of mole-percent, no difference could be found among the effects of the three alkalis. The alkalis were the only components found to significantly affect electrical conductivity. The alkaline earth oxides (Mg, Ca, Ba) caused the same types of behavior as did the alkali oxides, except

TABLE IV.1. Summary of Defense Waste Glass Study(a)

Oxide Components	Base Glass, wt%	Variation, wt%	Viscosity	Electrical Conductivity	Crystallinity	99°C Distilled Water(a)	pH-4(b)	pH-9	Devitrification
Li ₂ O	3.0	0-6.0	--	++	--	++	++	0	0
Na ₂ O	13.9	5.0-15.0	--	++	--	++	++	0	0
K ₂ O	0	0-6.0	--	++	--	++	++	0	0
MgO	0	0-3.0	0	0	0	+	++	0	0
CaO	4.53	0-6.0	--	0	-	0	++	0	0
BaO	0	0-3.0	0	0	0	++	++	0	-
U ₃ O ₈	1.53	0-4.0	0	-	-	-	0	0	0
TiO ₂	7.5	0-10.0	-	0	0	-	--	0	+
MnO ₂	2.58	1.16-4.0	0	0	+	-	+	0	0
Fe ₂ O ₃	7.9	0.39-15.41	-	0	++	0	+	0	+
NiO	0.53	0-3.0	+	0	++	0	0	0	0
ZnO	0	0-7.0	0	0	++	++	++	0	0
B ₂ O ₃	7.50	5.0-15.0	--	-	-	0	++	0	-
Al ₂ O ₃	11.60	1.56-21.64	++	-	++	-	++	0	++
SiO ₂	39.4	---						0	

(a) 0 indicates negligible change with increase in this component, + and - indicate increases or decreases; ++ and -- indicate large increases and decreases with component increase.

(b) + indicates an increase in leachability.

that they didn't greatly affect electrical conductivity. On a per-mole basis, the influence of alkaline earth oxides on the other properties was not as great and there was less uniformity in the effects they had upon the glass.

Titanium dioxide was the only component found to cause a large increase in pH-4 durability. It is of interest that it also caused a slight decrease in viscosity, since oxides that increase durability generally increase viscosity as well.

Aluminum, nickel and iron were all found to increase the formation of nickel-ferrite spinel crystals in the glass. The action of the aluminum is not well understood, as it is not found in the crystals. It may act by occupying sites in the glass structure that would otherwise be held by iron atoms. This could cause the iron to precipitate out of the glass structure to form the crystals. Crystallite formation was found to be more sensitive to concentrations of nickel than to those of iron. Additional details of the experiments and the results were previously presented (Mellinger and Chick 1979).

STATISTICAL DESIGN STUDY ON DEFENSE WASTE GLASSES

Attaining an understanding of glass properties in the compositional field shown in Table IV.2 was the objective of this study, which employed computer-aided statistical experimental design. The composition of the defense waste calcine is shown in Table IV.3. A computer program was used to choose 25 widely spaced test compositions lying on the boundaries of the composition field. The centroid and eight other compositions within the interior of the

TABLE IV.2. Composition Field for Defense Waste Study

Component	Low Value, mole%	High Value, mole%	Centroid Value, mole%
CaO	0	8	3.99
B ₂ O ₃	0	13	6.41
SiO ₂	36	51	43.50
Na ₂ O	15	35	25.60
Calcine	10	30	20.50

TABLE IV.3. Defense Waste Calcine Composition

Component	Wt%	Mole%
SiO ₂	3.85	8.04
Na ₂ CO ₃	1.16	1.37
CaCO ₃	7.51	9.41
Fe ₂ O ₃	48.94	38.40
Al ₂ O ₃	10.02	12.31
MnO ₂	13.01	18.74
NiO	6.17	10.34
Zeolite	8.09	0.29
Na ₂ SO ₄	1.25	1.10

field were also selected for testing. Among the properties determined were: 1) weight loss after 24 h in 99°C distilled water (Soxhlet) (Mendel et al. 1977); 2) weight loss after 19 h in buffered pH-4 solution at room temperature (pH-4) (Mendel et al. 1977); 3) temperature at which the viscosity was 100 poise; and 4) weight-percent of nickel-manganese-ferrite spinel crystals formed after a heat treatment of 1 h at 1150°C, 2 h at 1050°C, and 2 h at 900°C, followed by cooling with the furnace power shut off.

The data were fit to a partial cubic approximation model by least-squares analysis as a function of composition. These fitted models were used to predict the properties of glasses plotted in Figures IV.1 through IV.4. These figures show the predicted effects increasing or decreasing the level of a component from its level in the centroid composition (Table IV.2) has upon properties. The property value plotted at the 0% change point (where the curves intersect) is the predicted value for the centroid composition. As a component level is changed, the other component levels are adjusted but remain in the same proportions as in the centroid compositions. The magnitudes of the prediction-error standard deviations (error bars) shown demonstrate that curves which lie close together cannot be considered to be significantly different.

These "effects plots" illustrate the compromises necessary to balance acceptable final glass properties with processing practicality. For instance, reduction of Na₂O by 10 mole% would yield large improvements in chemical durability but would increase the melting temperature by almost 300°C.

FIGURE IV.1. Effects of Components on Soxhlet Leach Rate

FIGURE IV.2. Effects of Components on pH-4 Leach Rate

FIGURE IV.3. Effects of Components on Temperature at Which Viscosity = 100 Poise

FIGURE IV.4. Effects of Components on Weight-Percent Spinel

A review of spinel formation further illustrates the flexibility of interpretation that results from the development and use of approximation modeling for glass properties as a function of glass composition. None of the components in the full experimental design except for the waste calcine were found to have large effects upon the percentage of spinel crystals formed. Later, however, several additional glasses containing various levels of Li_2O were tested. A model was fitted that included Li_2O as a component, and Li_2O was discovered to have the effect of increasing the amount of spinel. Figure IV.5 is the effects plot that includes Li_2O . Figure IV.6, also developed from the Li_2O -containing model, shows the difference in predicted percent spinel versus calcine loading for a frit containing no Li_2O and for another with half of its Na_2O replaced by Li_2O . At the usual intended production calcine level of about 15 mole%, little or no spinel should form in either glass. However, if localized regions of glass containing higher amounts of calcine are formed in the melter as a result of inadequate frit and calcine mixing, significant amounts of spinel will form where the temperature is below the liquidus level. The lithium-containing frit will produce more spinel than will the frit without lithium.

Figure IV.7 is a graph of predicted viscosity at 1000°C versus calcine loading for the same two frits. As expected, at low calcine loadings the lithium-containing frit produces lower viscosities than does the frit without lithium. However, presumably as a result of increased spinel production, the lithium frit curve crosses and rises higher than does the curve without lithium at the higher calcine loadings. Comparison of Figures IV.6 and IV.7

FIGURE IV.5. Effect of SRP/TDS Study Components on Predicted Weight-Percent Spinel

shows that lithium-containing glasses with 30 mole% calcine could produce nearly 30 wt% spinel and have viscosities of roughly 1500 poise at 1000°C.

After localized agglomerations of spinel form in the melter, they can be expected to persist because of their high viscosities and resulting resistance to dissolution. They can also be expected to sink to the melter bottom because of their high densities.

FIGURE IV.6. Weight-Percent Spinel Versus Calcine Loading

FIGURE IV.7. Log Viscosity Versus Calcine Loading

ELEVEN-COMPONENT MIXTURE DESIGN STUDY ON GENERIC WASTE GLASSES

A study of the eleven-component waste glass system shown in Table IV.4 was begun using the experimental design and modeling methods described in the previous section. The increased number of components would result in the choice of unreasonable-extreme test compositions with properties beyond measurement ranges if the restrictions shown at the bottom of the table were not placed upon the allowable limits of the sums of glass network formers, modifiers, and intermediates.

Adequate modeling of this system will necessitate testing of approximately 70 compositions. Twenty-one have been tested so far and preliminary models of partial quadratic form have been developed. Figures IV.8 through IV.11 are the resulting effects plots. The magnitude of the prediction-error bars at this early stage precludes detailed interpretation. One surprising result is the apparent pronounced effect of chromium on Soxhlet leach rate, viscosity, and volatility.

Properties besides those shown in Figures IV.8 through IV.11 that will be studied on all or part of the melts will include devitrification and phase separation behavior, mechanical strength, thermal expansion, pH-4 leach rate, leach rate of specific elements, and radiation damage behavior.

TABLE IV.4. Composition Field for Eleven-Component Generic Study(a)

<u>Component</u>	<u>Low Value, mole%</u>	<u>High Value, mole%</u>	<u>Centroid Value, mole%</u>
<u>Formers</u>			
SiO ₂	42	58	49.03
B ₂ O ₃	6	12	8.82
Al ₂ O ₃	0	15	7.35
<u>Modifiers</u>			
Na ₂ O	11	16	13.24
CaO	0	14	6.86
MgO	0	8	3.92
<u>Intermediates</u>			
ZnO	0	6	2.94
TiO ₂	0	7	3.43
Cr ₂ O ₃	0	3	1.47
Fe ₂ O ₃	0	3	1.47
NiO	0	3	1.47

(a) 55 mole% ≤ Sum of Formers ≤ 75 mole%
14 mole% ≤ Sum of Modifiers ≤ 34 mole%
0 mole% ≤ Sum of Intermediates ≤ 22 mole%

FIGURE IV.8. Soxhlet Leach Rate Versus Change in Component from Centroid

FIGURE IV.9. Log Viscosity Versus Change in Component from Centroid

FIGURE IV.10. Log Conductivity Versus Change in Component from Centroid

FIGURE IV.11. Log Volatility Versus Change in Component from Centroid

FULL GENERIC STUDY

If the eleven-component study is successful, we plan to attempt a much larger compositional field designed to encompass all nuclear waste glasses. This full study would involve roughly 25 components and several hundred test melts.

V. ALTERNATIVE WASTE FORM DEVELOPMENT

J. M. Rusin, R. O. Lokken

Development of alternatives to the cast-glass waste form was initiated at PNL in 1973. The original objectives of this program were:

- to provide a backup or second-generation process;
- to produce a waste form that has improved durability and lower dispersibility;
- to produce inert forms from wastes not readily compatible with vitrification;
- to increase reliability through process simplification;
- to reduce the cost of solidification and/or storage.

It became apparent that the objectives of simplification and cost reduction could not realistically be achieved along with those of increased inertness. Thus, the primary goal of the program became to provide a backup or second-generation waste form of improved inertness.

The major effort from 1973 to 1978 was to develop alternative waste forms based upon a multibarrier concept, as shown in Figure V.1; these waste forms should not be confused with the engineered barriers discussed in Section III. This aspect of the multibarrier concept is designed to separate the radionuclide-containing inner core material from the environment by the use of coatings and metal matrices. The resultant composite waste form exhibits increased inertness due to improved thermal stability and mechanical strength, and the added barriers greatly improve leach resistance. Present development of the multibarrier concept was concluded this year by the production and characterization of four one-liter canisters that demonstrate various multibarrier concepts. The program will now be directed toward the characterization of other alternative waste form products. This will be achieved by a comparative study in which waste forms are characterized by standard tests and are compared to glass as the reference waste form. Reviews of waste processing methods and product characteristics have been published by Ross, Rusin and McElroy (1979); Rusin, Lokken and Wald (1979a); and Ross et al. (1979).

FIGURE V.1. Multibarrier Concept for Isolating High-Level Waste

MULTIBARRIER WASTE FORMS

Multibarrier waste forms have three major components: 1) the inner core particles that contain the radioactive waste; 2) an inert nonradioactive coating that is applied to each particle; and 3) a metal matrix around the cores that provides improved thermal conductivity, impact resistance, and in some cases, additional leach resistance.

Inner Core Development

Two options were developed for the inner core of the multibarrier concept: sintered-ceramic pellets and glass marbles.

Sintered-Ceramic Inner Cores

Sintered-ceramics are crystalline assemblages of mutually compatible, refractory, and leach-resistant solid-solution phases incorporating HLW ions. Supercalcine is one sintered-ceramic under investigation at Pennsylvania State University and PNL. Supercalcine powder is produced by spray-calcining liquid waste to which Al_2O_3 , CaO , SiO_2 , and SrO have been added.

Two synthetic mineral models (SPC-2 and SPC-4) have been developed for use as a core material of the multibarrier product (Rusin et al. 1978). The crystal chemical roles of waste ions are given in Table V.1. The formulae in this table are only nominal. Each of the nominal compositions has been synthesized separately and its x-ray diffraction pattern matched to the corresponding reflections in the diffractogram of the crystallized sintered-ceramic.

The major phases given in Table V.1 have been determined from more than 200 crystal chemical and compatibility studies (McCarthy 1977), but minor formation and the partitioning of

TABLE V.1. Crystal Chemical Roles of Waste Ions(a)

Ions	Nominal Composition Of Synthetic Mineral	Structure Type
$\text{Sr}, \text{Ln}^{(b)}$	$(\text{Ca}, \text{Sr})_2 \text{Ln}_8 (\text{SiO}_4)_6 \text{O}_2^{(c)}$	Apatite [A_{ss}]
$\text{Ln}, [\text{PO}_4]$	LnPO_4	Monazite [M_{ss}]
$\text{Cs}, \text{Rb}, \text{Na}$	$(\text{Cs}, \text{Rb}, \text{Na}) \text{AlSi}_2 \text{O}_6$	Pollucite [P]
Sr, Ba	$(\text{Ca}, \text{Sr}, \text{Ba}) \text{MoO}_4$	Scheelite [S_{ss}]
$\text{U}, \text{Ce}, \text{Zr}$	$(\text{U}, \text{Ce}, \text{Zr} \dots) \text{O}_{2+x}$	Fluorite [F_{ss}]
$\text{Zr}, \text{Ce}, \text{U}$	$(\text{Zr}, \text{Ce}, \text{U} \dots) \text{O}_{2+x}$	Tetragonal- Fluorite [T_{ss}]
$\text{Fe}, \text{Ni}, \text{Cr}$	$(\text{Ni}, \text{Fe}) (\text{Fe}, \text{Cr})_2 \text{O}_4$ and $(\text{Fe}, \text{Cr})_2 \text{O}_3$	Spinel [Sp_{ss}] Corundum [Fe_2O_3] _{ss}
Ru	RuO_2	Rutile

(a) $\text{Te}, \text{Pd}, \text{Rh}, \text{Tc}, \text{Pm}, \text{Np}, \text{Pu}, \text{Am}$, and Cm were not included in the simulated waste.

(b) $\text{Ln} = \text{La}, \text{Pr}, \text{Nd}, \text{Sm}, \text{Eu}, \text{Gd}, \text{Y}$.

(c) Additive ions are underlined. Strontium is also a waste ion.

ions among two or more phases is to be expected. For example, the rare earth ions are partitioned between the apatite and monazite phases, and a small amount may also be substituting in the fluorite and tetragonal-zirconia phases. The submicrometer dimensions of most of the crystals disqualify routine electron microprobe elemental characterization, but scanning transmission electron microscopy (STEM) will be utilized for direct characterization of elemental distributions in sintered-ceramic crystals in the near future.

From Table V.1 it can be seen that only four additives may be needed to tailor the liquid waste compositions: Ca, Al, Sr and Si. Nitrates of Ca, Sr and Al and colloidal silica are the liquid sources of these elements. Typically, twice the stoichiometrically required level of additives are specified, because the day-to-day waste stream compositions are expected to vary considerably. The extra Ca would fix transient excesses of Mo, and the combination of Al and Si serves the same purpose for the alkali elements. If the excess additives are not completely combined with waste constituents, they form an inert but generally x-ray-amorphous calcium-aluminosilicate phase.

Process simplicity, advanced stages of process development, demonstrated operating capability, and highly desirable calcine powder characteristics make the spray calciner ideally suited to the production of a reactive amorphous powder. The amorphous spray-calcined powder consists of metal oxides, a trace of moisture and some residual nitrates or carbonates, depending upon feedstock composition. The powder is very fine and typically displays surface areas of 10 to 20 m²/g.

Consolidated pellets are produced from the amorphous spray calcine powder by disc-pelletizing. Disc-pelletizing is an agglomeration technique that forms spherical pellets from powders (Floyd and Engelleitner 1967). The purpose of pelletizing the spray-calcined powder was to produce consolidated, high-density spheres (pellets) about 1 to 7 mm in dia that can be sintered and crystallized by subsequent heat treatment.

The sintering behavior of supercalcine was studied to identify parameters to be used in the densification and crystallization of sintered-ceramic pellets and to identify differences in sintering behavior among various preparation techniques and/or formulations. Two methods were used--one incorporating a bulk-vibrated sample with a density typical of disc-pelletizing, and the other a pressed sample representative of standard sintering tests.

For the bulk test, alumina crucibles were filled and vibrated to produce powder samples with densities comparable to that of pelletized supercalcine (0.90 to 1.15 g/cm³). The second series of sintered samples was produced by pressing as-prepared calcine powder at 3400 psi in a 0.75-in. steel punch and die. Table V.2 summarizes the sintering information for pressed, vibrated, and disc-pelletized calcine.

The resulting pelletized sintered densities were within experimental error of the values obtained for the vibrated sintered samples. Thus, the vibrated samples were used to determine proper process conditions.

Glass Marble Inner Cores

Glass marbles provide an alternative to the cast glass waste form but do not require the development of a new waste form material. Marble production would provide a separate step

TABLE V.2. Sintered Density of Sintered-Ceramics

<u>Material and Treatment</u>	<u>Sintering Temp., °C</u>	<u>Bulk Sintering Density, g/cm³</u>
SPC-2, pressed	1100	3.22
SPC-4, pressed	1200	4.21
SPC-2, vibrated	1170	3.84
SPC-4, vibrated	1230	3.68
SPC-2, pelletized	1175	3.84
SPC-4, pelletized	1230	3.60

between the melter and the canister to allow for quality assurance and ease of recycling to the melter if a below-standard product is produced.

The technique used to produce simulated waste glass marbles for multibarrier development is a laboratory-scale version of a process developed by Knapp and Smith (1962). The process incorporates the direct casting of a glass stream into vibrating molds. The cavities in the molds are conical and have hemispherical bottoms.

Coating Development

The development of coatings for sintered-ceramics was pursued to provide an additional protective layer between the radionuclides and the environment. The chemical vapor deposition (CVD) coatings include the application of a 40- μm pyrolytic carbon (PyC) layer as a barrier to increase leach resistance and a 60- μm Al_2O_3 layer as a barrier to increase oxidation resistance. Glass coating of sintered-ceramics by frit and glaze, which is a less complex coating process, was also investigated. Although coatings offer increased inertness, a high level of technological complexity is also required.

Several approaches were explored at the Battelle-Columbus Laboratory in an effort to overcoat PyC-coated sintered-ceramic particles with a metal oxide. The PyC coating was deposited from decomposition of C_3H_8 or C_2H_2 in a fluidized bed. The primary function of the PyC layer is to provide leach resistance in water. The metal-oxide coating protects the PyC layer from oxidation at elevated temperatures and also provides additional leach resistance.

Fluidized-Bed Coatings of PyC/ Al_2O_3

In preliminary work, SPC-2 sintered pellets were overcoated with PyC and Al_2O_3 in a fluidized bed with ZrO_2 diluent as an expedient way of supplying materials for testing. This method yielded good-quality Al_2O_3 and PyC coatings on 20-g beds of particles, but the Al_2O_3 coatings were only successful when the particle size was less than 2 mm. The modifications necessary to extend this process to beds of more economical size containing larger particles (>2 mm) were not justified in comparison to simpler approaches. Consequently, the application of Al_2O_3 coatings in a drum coater were explored.

Drum-Coating

Good-quality protective coatings were obtained by drum-coating. The procedure first involved overcoating the PyC with SiO_2 , which then protected the PyC layer during

application of an impervious layer of Al_2O_3 . The negative feature of this approach was that two chemically different oxide layers were required. Because of this complication in the drum-coating system, a vibrating-bed system was examined.

Alumina Overcoating of PyC in a Vibrating Bed

Alumina overcoating in a vibrating bed of PyC-coated sintered-ceramic cores (2- to 3-mm) was successfully applied to beds of $\sim 100 \text{ cm}^3$. This method was used to overcoat $\sim 1100 \text{ cm}^3$ of PyC-coated sintered-ceramic cores for matrix encapsulation tests. The PyC coatings had been applied previously by the fluidized-bed method.

Laboratory-Scale Production of Inert Glass Coatings

Two techniques to produce inert glass coatings were examined on a laboratory scale. In both cases a coating material of glass frit or glaze slip was applied to sintered-ceramic spheres at room temperature and heated to form a continuous glass coating over the sphere surface.

In the first technique a ground frit coating up to 1 mm thick was applied to sintered-ceramic spheres 5 mm to 10 mm in dia using the disc pelletizer. The technique was similar to that used in the pharmaceutical industry to coat pills. The sintered pellets were placed in the rotating pelletizer, and a quantity of frit and a fine water spray were simultaneously added.

In the second technique, spraying or dipping methods were used to apply the glaze slip to sintered spheres. While spraying has considerable process advantages and was quite promising, it required tight control of slip properties. Dipping is a more complex process, but it was not as sensitive to the fluctuating slip properties that were encountered. Good-quality glass coatings were produced by both options. Scaleup of such processes to a remote scale may be difficult, however.

Metal-Matrix Development

Two types of processes were considered for the encapsulation of solidified HLW: sintered-metal powders and vacuum-cast alloys. Selection of these processes is based on the compatibility of different metals with the advanced waste particle forms, the ease of the encapsulation process, and the optimization of high thermal conductivity, impact strength, and corrosion resistance.

Sintered-Metal Powder

Sintered-metal powders are considered to be prime candidates for use as metal matrices with sintered-ceramic pellets. This combination allows high levels of heat generation and the highest allowable fabrication and storage temperatures. The primary reason for considering sintered matrices is that metals with high melting points can be employed (e.g., copper, bronze, stainless steels, etc.). The potential loss of a matrix during a high-temperature accident is thus reduced. Sintering also lends itself well to remotely operated fabrication facilities because the process is fairly simple.

Since sintered matrices are formed from near-spherical metal particles, final matrix densities range from ~40% to ~65% of theoretical density. Compared to the cast, 100%-dense metal matrices, sintered matrices may not offer the optimum leach protection and thermal conductivity because of the interconnecting porosity of the sintered matrix.

Vacuum-Cast Alloys

Vacuum-cast alloys are considered to be prime candidates for matrix encapsulation of waste-glass marbles and glass-coated or uncoated sintered-ceramics. Fabrication temperatures for the glass marble and glass-coated sintered-ceramic waste forms are limited by the softening points of the glasses, which are ~600°C. Uncoated sintered-ceramics can have a fabrication temperature limit of 1200°C, which is above the casting temperature of some candidate metal-matrix materials. Vacuum-cast matrices have many advantages over the sintered matrices, since the matrix will be cast at 100% density.

Lead, lead alloys, aluminum and aluminum alloys are the best candidates for vacuum-cast matrices because of fabrication temperature restrictions and their relatively low melting temperatures. Aluminum and its alloys have higher thermal conductivity values, higher melting points, and greater strengths than do the lead alloys but may have lower long-term chemical durabilities. Although a greater density of lead provides increased radiation shielding, the increased weight may add some difficulty in handling and transporting the canisters.

ONE-LITER DEMONSTRATIONS

Four multibarrier concepts were demonstrated on a one-liter scale: 1) glass marbles in a lead-tin matrix, 2) sintered supercalcine pellets in an aluminum-silicon matrix, 3) sintered supercalcine pellets coated with glass in an aluminum-silicon matrix, and 4) supercalcine pellets coated with pyrolytic carbon and aluminum oxide in a copper matrix. The development and characterization of these concepts has been described elsewhere (Rusin et al. 1978; McCarthy 1977; Floyd and Engelleitner 1967; Chapman 1976; Knapp and Smith 1962; Rusin, Lokken and Wald 1979b).

In general, proposed waste form processes have properties that fall within a narrow range (Rusin 1978). Process complexity and feasibility therefore become important parameters.

Based upon the development and characterization studies at PNL, several conclusions can be made:

- Sintering and vacuum-casting are both applicable methods for metal-matrix encapsulation.
- The multibarrier concept of glass marbles being encapsulated in a vacuum-cast lead alloy provides improved inertness with the smallest increase in technological complexity.
- If it were desirable to develop a crystalline multibarrier waste form, uncoated sintered-ceramic pellets would require a much lower level of technological complexity than would glaze- or CVD-coated pellets.

- The 16-in.-dia pelletizer unit has enough capacity to handle the output of a large PNL spray calciner (~50 kg calcine/h) and it can form spray-calcined material into 2- to 20-mm-dia pellets that are strong enough to withstand handling without significant breakage.
- Chemical-vapor-deposition coating of sintered-ceramics should be pursued only if a very high level of inertness is required.

VI. PRIMARY WASTE FORM CANISTER

S. C. Slate

Waste forms are generally contained within a metallic canister. This canister has the primary function of containing the waste form and facilitating handling during processing, interim storage and disposal. It is not currently viewed as a long-term barrier in the repository. The development and selection of materials for use as a long-term (>1000-yr) containment has begun, but the data is not included in this year's report because of its preliminary nature.

The waste form canister is a significant part of the waste package, and interactions between it and the waste form have been evaluated and discussed in earlier documents (Slate and Ross 1977, Slate et al. 1978). The majority of experience with canisters has been related to the containment of waste glass. Criteria for waste canister design are currently being developed as part of the Commercial Waste Packaging studies. A preliminary draft of these criteria is available (Moore 1978). The criteria address the matters of licensing, physical dimensions, radiation limits and quality control.

Reference canister designs have been developed at PNL for both the in-can melting (ICM) and continuous melting (CM) processes. The basic design consists of a single-wall pipe with a flat, flanged bottom. The top will probably also be flat, though it may be domed on large-diameter canisters. The top of the canister has a carefully designed opening that couples with the vitrification equipment and allows for a reliable final closure.

The diameter of the canister will range from 30 cm to 91 cm, and its length will be about 3 meters. The canisters are currently made of either stainless or carbon steels. The current reference stainless-steel alloys are 304L and Inconel-601, though other alloys are also being studied. Figure VI.1 shows the current PNL reference designs for ICM and CM canisters. These designs are intended for low-heat wastes. The ICM canister has internal fins that are utilized to achieve the high melting rates desired for large-scale production rates. Fins can also be used in either design for improved heat transfer through the glass when using high-heat wastes.

The research at PNL on waste canisters is directed toward three main areas. The first is technology development, which is where the basic data and analytical techniques necessary to design a canister are developed. The second is testing of full-scale canisters using prototype vitrification equipment. The third is canister processing development, which involves the study of canister-handling operations.

TECHNOLOGY DEVELOPMENT

We are determining basic design properties of potential canister materials and analytical methods for predicting canister performance. Capabilities for predicting thermal and structural performance have already been developed.

FIGURE VI.1. Two Reference ICM Canister Designs

Materials

The evaluation of materials is one of the most important development activities. We are studying several material properties: strength (over a temperature range of 100⁰ to 1150⁰C), corrosion resistance, ease of fabrication, cost, and long-term stability. The major areas of study have been concerned with corrosion resistance and material strength. The corrosion rates of several canister materials in different glass compositions have been reported (Slate and Maness 1978). Work has continued subsequent to that report using new glass compositions. We have measured the strength of 304L and Inconel-601 at temperatures

between 900°C and 1150°C and have reported the data (VanEcho and Simonen 1978). These data on high-temperature strength are necessary in predicting the performance of the canister during the ICM process.

Stress Analysis

A document summarizing all the stress analyses conducted on the primary storage canister over the last several years has been recently completed (Simonen and Slate 1977). The subject of the report is the structural integrity of waste canisters during processing, handling, interim storage, and transportation.

We have analyzed stresses in canisters and evaluated integrity under projected service loadings. The loadings canisters experience are from lifting and handling, internal pressure, high-temperature filling operations, transient heating and cooling, the differential in thermal expansion coefficients of the canister and glass, and impact loadings from low-probability accidents. Case studies are included that analyze these service loadings, illustrate applicable stress analysis methods, show preferred design approaches, and provide useful engineering design data.

Thermal Analysis

The prediction of the thermal performance of the glass/canister system is important in assuring glass quality and canister integrity and in making design judgments. Early work on the thermal analysis of canisters was reported in the first Waste Fixation Program annual report (Mendel et al. 1977). Since that time we have improved the computer model and have correlated its results with experimental data.

An advanced 2-D computer model was developed at PNL to explicitly model the cross section of a canister containing internal fins. The model is very flexible and can predict canister temperatures under a wide variety of conditions.

A new area in our thermal analysis work is the interpretation of empirical temperature data from full-scale canister tests. We are using this data to evaluate the accuracy of our computer model. One of the biggest questions about the accuracy of our model is how well it can predict the thermal performance of cracked glass that is found in the large canisters. So far, preliminary results indicate that cracking does not significantly affect the transfer of heat from the glass to the outside.

A brief discussion of the computer model and the analysis of empirical data is presented in a paper by Wescott and Slate (1979).

FULL-SCALE TESTING

The data from the technology development task is used to design full-scale canisters. These canisters are then filled with glass using the full-scale vitrification equipment. The goal of these tests is to verify the performance of the canister under normal and accident conditions. Full-scale testing of vitrification equipment has been conducted on a regular

basis at PNL since 1977. To date, 25 canisters have been filled by the ICM process and 50 canisters have been filled by the CM process. These canisters have ranged from 30 to 91 cm in dia and from 2.1 to 3.0 m in length.

During these tests we gather data on the performance of the canister. Temperature data are the most important kinds of information to be gained, because they are useful in predicting corrosion and mechanical deformation and in understanding the final chemical and mechanical condition of the glass. Both absolute temperatures and temperature gradients are measured on the canister and in the glass.

Temperature Data

An example of the data taken is shown in Figure VI.2. This figure shows the radial temperature profile in a 60-cm-dia canister as a function of time. This information is useful in estimating cracking and in analyzing the condition of the glass. We are now analyzing the large volume of data we have accumulated from all the full-scale tests.

Canister Corrosion and Deformation

We have evaluated corrosion and mechanical deformation. Corrosion of the canister is measured by examining a sample of the actual canister wall. Canister distortion is determined by finding the change in canister diameter at various heights. In general, insignificant distortion is seen in CM canisters, and there is only an increase of ~1% in the diameter of an ICM canister. Two major full-scale tests are described by Chapman (1979) and McElroy et al. (1979b).

FIGURE VI.2. Radial Temperature Profiles of a 60-cm-dia Ceramic Melter Canister of Glass as a Function of Time

Impact Tests

Full-scale canisters have been used in evaluating canister performance in impact tests. A total of 13 canisters that ranged from 30 cm to 60 cm in dia were dropped from heights ranging from 6 m to 30 m (McElroy et al. 1979c). The drop-test results are discussed by Simonen and Slate (1977). These authors conclude that canisters of simple design can sustain severe impacts to the bottom or side. The effect the impact has on the glass is discussed in Section X.

Canister Overheat Test

We have also simulated a loss-of-cooling accident that might occur during the ICM process. The most serious ICM accident possible would have a canister overheating as a result of the self-heating nature of the glass. In this test we evaluated the canister performance and the effect high temperature has on the glass. Temperatures were measured for correlation with the heat transfer computer model. To simulate the internal heat generation, we used direct joule-heating of the fins inside a 20-cm-dia canister.

A maximum power input of 25 kW was used during the test. At this level the canister reached a maximum temperature of 900°C and the glass reached an average of 1350°C. The glass near the fins probably reached about 1450°C, but this was not confirmed by a direct measurement. The test ended when an internal fin failed because of corrosion. The most important result from this test is that even at these elevated temperatures the glass was not significantly altered, and there was no sign of a reboil phenomenon. Nor were any significant effects noted on the canister.

CANISTER PROCESSING OPERATIONS

The major processing operations that a waste canister must experience going from fabrication through to terminal storage are being studied. Fourteen major operations have been identified. We have already demonstrated several of these process steps: filling and cooldown with the full-scale equipment and canisters, seal-welding, and helium leak inspection of our twist-lock lid closure (McElroy et al. 1979d). A full-scale water storage experiment to test the long-term corrosion behavior of prototypic (although nonradioactive) canisters of glass is in progress. Canisters are stored in 1- to 1000-ppm chloride water at 50° to 80°C. No significant effects have been observed after the first 8 mo of water storage.

VII. LEACHING STUDIES

J. H. Westsik, Jr., D. J. Bradley, Y. B. Katayama, R. P. Turcotte

During 1978 the scope of the leaching studies at PNL continued to broaden. In addition to leach-testing of glass done in support of the HLWIP development and characterization activities, testing of alternative waste forms and spent fuel is under way. The long-term testing of spent fuel originated in the Waste Fixation Program (WFP), and this year continued under the Waste Isolation Safety Assessment Program (WISAP). The WISAP is also investigating the behavior of HLW glass in environments simulating geologic repositories.

GLASS LEACHING

Long-term leach tests continue as an integral part of the glass characterization studies. High-temperature tests were initiated to accelerate the leaching process so that the future leaching behavior of the glass can be estimated.

Long-Term Leach Tests

Long-term leach tests are used for two reasons: 1) to quantify the leaching process, and 2) to characterize the effects of thermal treatment or radiation exposure on the glass. Typically, a modified IAEA leach test is used (Mendel et al. 1977). Table VII.1 lists the latest leach rates measured for crushed samples of the four simulated commercial power waste glasses (72-68, 76-68, 77-107, 77-260) leached in 25°C deionized water. These bulk glass leach rates based on Cs and Sr continue to decrease with time. Part of the decrease for the 76-68 and 72-68 glasses may be a result of an increase in the leaching period from 28 to 180+ d, as discussed in PNL-2625 (Ross et al. 1978). As shown in Figure VII.1, after more than 1000 d of leaching the leach rates of 72-68 glass continue to decrease in a completely static system, as compared to a system where the leachant is changed according to the IAEA method.

In another test we determined how changes in cesium and strontium concentration in 76-68 glass can affect the leach rate. Samples of 76-68 glass in which the cesium and strontium concentrations varied by factors of 0.1, 0.5, 1.0, 2.0, 5.0 and 10.0 from the defined concentrations were leached using the modified IAEA procedures. Leach rates based upon cesium releases from the crushed glass are plotted in Figure VII.2. These are average leach rates over the time from 7 through 119 d of exposure to 25°C deionized water. In the range from 0.5 to 5.0 times the defined concentrations, leach rates remain constant. This means that

TABLE VII.1. Latest Long-Term Leach Rates of Four Simulated HLW Glasses

Glass	Total Time Leached, d	Latest Leaching Interval, d	Leach Rate, g glass/cm ² -d (based on Cs and Sr)	
			Cs	Sr
72-68	1173	184	5 x 10 ⁻⁸	7 x 10 ⁻⁸
76-68	596	183	6 x 10 ⁻⁹	6 x 10 ⁻⁹
77-107	230	28	6 x 10 ⁻⁹	3 x 10 ⁻⁷
77-260	231	28	2 x 10 ⁻⁸	6 x 10 ⁻⁸

FIGURE VII.1. Comparison of Static and IAEA Leach Test Results

FIGURE VII.2. Leach Rates of 76-68 Glass Based on Cesium as a Function of the Cesium Concentration in the Glass

more cesium and strontium are released from the glasses that contain higher concentrations of them. However, the fraction released of each element (and therefore the leach rate) remains constant. The changes in the glass composition at 0.1 and 10.0 times the defined Cs and Sr loadings changed the glass structure such that the leach rates increase at these extremes. It also emphasizes that reduced waste loadings will not necessarily reduce the leach rate of the glass: glasses 72-68 and 77-107 have higher leach rates than do 76-68 and 77-260.

Both the Soxhlet and the long-term leach tests are used to evaluate the changes in chemical durability of a glass due to long-time thermal anneals. Figures VII.3 and VII.4 show average long-term leach rates of 77-107 and 77-260 glasses based on their releases of cesium and strontium. Before leaching, the samples were stored in air at a series of temperatures between 300⁰ and 900⁰C for 60 days. After quenching, the samples were crushed to -42 and 60 mesh before the 25⁰C test. The figures show average leach rates from 22 through 231 d as a function of the storage temperature. The two glasses show only minor changes in leachability resulting from the thermal treatments. Glass 77-260 does show a spike in its Sr-based leach rate at the 700⁰C storage temperature. When these curves are compared with Figure 17 in PNL-2625 (Ross et al. 1978), it is apparent that the glass composition typically has more influence on its leach rate than does the thermal treatment.

One-year storage samples of 77-107 and 77-260 glasses were tested using the 72-h Soxhlet test. Table VII.2 shows the results of these 99⁰C tests. These weight loss measurements should be compared with those for shorter storage times shown in Table 8 in PNL-2625 (Ross et al. 1978). While 77-260 glass is slightly more affected than is 77-107, both glass formulations have very good thermal stabilities over the entire devitrification temperature range.

The WISAP program is using, among others, the long-term test to generate elemental release rate data specifically oriented toward geologic disposal conditions. Samples of 76-68 glass doped with tracer quantities of Tc, Am, U, Pu, Np, and Cm were leached in a salt brine, deionized water, and solutions of calcium chloride, sodium bicarbonate and sodium chloride. Figures VII.5 and VII.6 show leach rates of the glass based on ²³⁹Pu releases. Curium and neptunium results follow the same trends. There is about a factor of 10 difference between the leach rates obtained in salt brine and in the bicarbonate solution. The other three solutions fall inside this band.

Hydrothermal Studies

Leaching studies of nuclear waste glasses have usually been conducted at or below 100⁰C. We have extended these studies to higher temperatures so that we can: 1) provide accelerated test conditions, and 2) establish reaction rates over a broad temperature range. Many of the results presented here are discussed in more detail in PNL-2759 (Westsik and Turcotte 1978). Studies with a supercalcline and Cermet are discussed later in this section.

In these hydrothermal studies of 76-68 glass, a solid glass cylinder, some powdered glass, some powdered geologic material, and deionized water in the mass ratio 1:5:50:63 were reacted at 350⁰C for one and three weeks. The geologic material was either crushed salt or crushed Umtanum basalt. The temperature used is significantly higher than would be expected in a wet repository. It was used in these tests only to accelerate the rates of reactions.

FIGURE VII.3. Average Long-Term Cesium Leach Rates for 77-107 and 77-260 Glasses(a)

(a) Samples stored two months.

The waste glass undergoes various levels of crystallization, depending upon the exposure conditions. The primary reconstruction product is $\text{NaFeSi}_2\text{O}_6$. Metallographic examination of the glass cylinders reveals that the rate of alteration is highest in deionized water, followed by the basalt system and finally the salt brine. However, Table VII.3 shows that under equivalent test conditions much more cesium, rubidium and strontium are released from the powdered glass to the salt brine than are released to deionized water or the basalt system. Releases

FIGURE VII.4. Average Long-Term Strontium Leach Rates for 77-107 and 77-260 Glasses(a)

(a) Samples stored two months.

were lowest in the basalt system, through some of the ions leached from the glass may have reprecipitated on the glass or may have reacted with the basalt as it also altered. Since the solution concentrations are relatively constant between the 7-d and 21-d tests in salt brine or deionized water, the leaching of the glass is apparently being limited by solubility of the leached elements in these systems.

TABLE VII.2. Soxhlet Leach Data for Standard Glasses After One-Year Thermal Storage^(a)

Storage Temperature, °C	Glass 77-107	Glass 77-260
300	1.93	3.07
400	3.11	3.50
500	2.87	2.77
550	2.08	2.79
600	2.69	2.21
650	3.35	2.50
700	3.16	4.00
750	2.37	3.88

(a) Leach rate in percent weight loss in 72 h; convert to $\text{g}/\text{cm}^2\text{-d}$ by multiplying by 1.28×10^{-5} .

FIGURE VII.5. Long-Term Leach Test Results in Brine, Bicarbonate and Deionized Waters

FIGURE VII.6. Long-Term Leach Rates in CaCl_2 and NaCl Solutions

TABLE VII.3. Hydrothermal Leach Test Results for 76-68 Glass

Solution	Time, d	Leach Rate Based on Weight Loss, $\text{g/cm}^2\text{-d}$ (a)	Concentration of Element in Solution, mg/l (b)							
			(% released in parentheses)							
			Cs	Rb	Sr	Mo	Si	B	U	Zn
Brine	7	4.0×10^{-3}	650 (66)	87 (72)	11.6 (3.6)	830 (54)	35 (0.2)	2100 (71)	1.5 (<0.1)	21 (0.5)
Brine	7	4.6×10^{-3}	760 (80)	96 (82)	10.6 (3.4)	880 (59)	33 (0.2)	2100 (73)	0.2 (<0.1)	10 (0.3)
Brine	21	4.5×10^{-3}	990 (95)	115 (90)	16.5 (4.8)	1010 (62)	47 (0.2)	3000 (96)	0.5 (<0.1)	13 (0.3)
Brine	21	(c)	650 (70)	111 (96)	10.4 (3.4)	(c)	24 (0.1)	2500 (89)	6.3 (0.2)	23 (0.6)
Deionized Water	7	5.3×10^{-3}	65 (6)	20 (16)	0.63 (0.2)	780 (49)	420 (2.2)	3400 (100)	4.8 (0.1)	0.33 (<0.1)
Deionized Water	21	4.0×10^{-3}	37 (4)	24 (20)	1.27 (0.4)	940 (63)	340 (1.9)	2500 (86)	8.5 (0.2)	1.6 (<0.1)
Basalt System	7	(c)	2.2 (0.10)	0.30 (0.12)	0.48 (0.07)	55 (1.7)	25 (0.06)	160 (2.5)	0.34 (0.0004)	(c)
Basalt System	21	(c)	0.82 (0.04)	0.15 (0.06)	0.31 (0.05)	1.6 (0.05)	27 (0.07)	360 (5.9)	0.12 (0.002)	(c)

(a) Weight loss of a cylinder of material divided by its geometric surface area and time.

(b) Each test included roughly 20% by weight of a solid cylinder and 80% -325 mesh powder.

The majority of ions in solution were leached from the powder.

(c) Not available.

ALTERNATIVE WASTE FORMS

Supercalcine

In autoclave tests similar to those for 76-68 glass, supercalcine has been exposed to hydrothermal conditions. Twelve grams of SPC-4 supercalcine powder, a hot-pressed pellet, and a sintered pellet of supercalcine were reacted with 150 ml of deionized water at 350°C for 21 days. In one test, 120 g of crushed NaCl were included to give a saturated salt brine solution.

Table VII.4 lists the results of the solution analyses for these tests in salt brine and deionized water. Also included are data from a 3-d test shown originally in Table 3 of PNL-2759 (Westsik and Turcotte 1978). The concentrations of Cs, Rb and Sr released to the salt brine are higher from supercalcine than from the 76-68 glass discussed earlier. However, since SPC-4 supercalcine has a higher fission-product loading than does the glass (63.2% vs. 12.8%), the fraction of these fission products in solution is comparable for the two waste forms. Solution concentrations in deionized water are generally lower than are concentrations in salt brine.

We were able to obtain only one weight loss measurement from the hot-pressed and sintered pellets. The hot-pressed pellet treated 21 d in deionized water showed a weight loss rate of 6.2×10^{-4} g/cm²-d. The other pellets either broke as they were removed from the autoclave, or else some of the loose powder reacted and adhered to the pellet surface.

Figure VII.7 shows cross sections of the four pellets. Despite the large releases to the salt brine, the hot-pressed and sintered pellets from these tests do not appear to have an alteration layer. The pellets treated in deionized water do show an alteration layer, although the thicknesses are not constant. The maximum thickness is 0.075 cm for both the hot-pressed and the sintered pellets.

TABLE VII.4. Leachability Results of Supercalcine Autoclave Tests

<u>Solution</u>	<u>Time, d</u>	<u>Leach Rate Based on Weight Loss, g/cm²-d^(a)</u>	<u>Concentration of Element in Solution, mg/l^(b)</u> <u>(% released in parentheses)</u>				
			<u>Cs</u>	<u>Rb</u>	<u>Sr</u>	<u>Mo</u>	<u>Si</u>
Brine	3	(c)	2210 (46)	487 (80)	52.5 (3.3)	40 (0.6)	49 (0.5)
Brine	21	(c)	5700 (54)	1200 (89)	59 (1.7)	7.7 (0.1)	31 (0.2)
Deionized Water	21	6.2×10^{-4}	20 (0.3)	11 (1.3)	4.8 (0.2)	34 (0.4)	25 (0.2)

(a) Weight loss of a cylinder of material divided by its geometric surface area and time.

(b) Each test included roughly 20% by weight of a solid cylinder and 80% -325 mesh powder.
The majority of ions in solution were leached from the powder.

(c) Not available.

FIGURE VII.7. Cross Sections of Hot-Pressed and Sintered Supercalcine Pellets Exposed to Hydrothermal Conditions

Oak Ridge National Laboratory Cermet

The chemical durability of the Oak Ridge National Laboratory (ORNL) Cermet waste form was evaluated using the Soxhlet, pH-4, pH-9, IAEA, and autoclave leach tests. The thick discs were doped with ^{137}Cs and ^{106}Ru at ORNL. Leach rates were then determined using these isotopes and weight loss measurements. The results are shown in Table VII.5.

The Cermet is defined as a continuous iron-nickel metal phase containing small particles of waste oxides (Aaron et al. 1978). In preparing the Cermet, many of the fission products, including ruthenium, are reduced to their metallic states. Cesium is incorporated in a

TABLE VII.5. Results of Leach Tests on ORNL Cermet

Leach Test	Conditions	Weight Loss	Leach Rate, g/cm ² -d	
			¹³⁷ Cs	¹⁰⁷ Ru
Soxhlet	99°C, 72 h; Distilled H ₂ O	7.1 x 10 ⁻⁶	7.2 x 10 ⁻⁵	(a)
pH-4	25°C, 31 h; Acetate Buffer	7.4 x 10 ⁻⁴	4.6 x 10 ⁻⁴	1.0 x 10 ⁻⁵
pH-9	25°C, 31 h; Ammonium Hydrox- ide Buffer	1.6 x 10 ⁻⁵	2.4 x 10 ⁻⁴	1.7 x 10 ⁻⁶
IAEA	25°C, 146 d; Deionized H ₂ O	4.1 x 10 ⁻⁶	4.3 x 10 ⁻⁶ (average over 146 d)	(a)
Autoclave	350°C 7 d; Deionized H ₂ O	1.5 x 10 ⁻⁵	1.5 x 10 ⁻²	(a)
Autoclave	350°C 7 d; Saturated NaCl	Gained Weight	3.9 x 10 ⁻²	(a)

(a) Not detected.

pollucite phase within the metal matrix. The discs we received for leach-testing had mirror surfaces with some slight imperfections--apparently from the waste oxides. Those discs leached at room temperature retained their shiny surfaces after the test. There was a galvanic reaction between the Cermet and the stainless steel baskets used to hold the sample in the pH-4, pH-9, and IAEA leach tests. Rust-colored patches on both the samples and the baskets resulted from this galvanic reaction. Oak Ridge is looking at these samples to determine the changes in the Cermet. The two samples exposed to hydrothermal conditions in a Hastelloy autoclave had dull gray surfaces at the end of the test, but they did not show any rust coloring. The gray finish is probably a thin oxide coating.

The leach rate data do not show any surprises. Ruthenium is less mobile than is cesium and, as such, is not detected in most of the tests. Cesium releases increased with increasing temperature--from 4×10^{-6} at 25°C to 7×10^{-5} at 99°C to 1.5×10^{-2} g/cm²-d at 350°C. This corresponds to an activation energy of 1 kcal/mole. Releases of cesium at a given temperature increase as the ionic strength of the solution increases. The pH-4 and pH-9 test results, when compared with the IAEA test and the two autoclave test results, support this conclusion. Because of the galvanic reaction and the oxide film formation, the leach rates based on weight loss probably do not reveal much about the leaching behavior of the Cermet.

SPENT FUEL

Spent LWR fuels have been leach-tested to determine the effects of time and burnup on the chemical durability of the fuel. This work originated in the Waste Fixation Program in 1975,

but is now being funded by the WISAP as part of their spent fuel studies. This work is reported in detail in PNL-2982 (Katayama 1979).

Spent LWR fuels with burnups of 9.0, 28.0 and 54.5 MWd/kgU have been leach-tested in deionized water at 25°C in the Paige leach test apparatus (Mendel et al. 1977). Burnup has no effect upon the leach rates based on ^{137}Cs and 239 & ^{240}Pu releases, as shown by Figures VII.8 and VII.9. The leach rates based on uranium do appear to be influenced by the burnup of the fuel, as is seen in Figure VII.10. Differences in the physical structure of the fuels may have caused the differences. Light optical examination showed that the low-burnup fuel had less porosity than did the higher-burnup fuels. This is a function of the fabrication and irradiation history of the fuel.

Figure VII.11 shows the leach rate curves based on ^{244}Cm . The low-burnup fuel (9.0 MWd/kgU) has a leach rate approximately 50 times greater than does the high-burnup fuel (54.5 MWd/kgU). These leach rates are in the reverse order of the curium concentration in the fuel predicted by ORIGEN (Bell 1973), where 54.5-MWd/kgU fuel contains 1000 times the curium concentration of 9.0-MWd/kgU fuel. After 350 d of cumulative leaching, the curves for the three different fuels converge and are within the one-order-of-magnitude experimental uncertainty range. The large differences in ^{244}Cm leach rate are short-term when measured on a waste isolation time scale (thousands of years).

A long-term leach effect has been observed with the 54.5-MWd/kgU-burnup spent fuel exposed to deionized water at 25°C. A rise in the leach rates was observed after approximately 600 d of cumulative leaching, and it is shown in Figure VII.12. During the rise, the leach rates for all the measured radionuclides become nearly equal. Evidence suggests that exposure of new surfaces to the leachant may cause the increase. As a result, a study of spent fuel leaching mechanisms has been initiated.

FIGURE VII.8. Leach Rate of Spent Fuels Based on Release of ^{137}Cs in Deionized Water at 25°C with Burnups of 9.0, 28.0 and 54.5 MWd/kgU

FIGURE VII.9. Leach Rate of Spent Fuels Based on Release of 239 & 240Pu in Deionized Water at 25°C with Burnups of 9.0, 28.0 and 54.5 MWd/kgU

FIGURE VII.10. Leach Rate of Spent Fuels Based on the Release of Uranium in Deionized Water at 25°C

FIGURE VII.11. Leach Rate of Spent LWR Fuels Based on the Release of ^{244}Cm in Deionized Water at 25°C with Burnups of 9.0, 28.0 and 54.5 MWd/kgU

FIGURE VII.12. Leach Rate of 54.5-MWd/kgU Spent LWR Fuel in Deionized Water at 250C(a)

(a) Duplicate Samples are Designated Z-6 and Z-7.

VIII. PHASE BEHAVIOR AND THERMAL EFFECTS

R. P. Turcotte, J. W. Wald and R. P. May

The development of nuclear waste solids requires evaluation of the product with respect to general physical integrity and the composition and concentration of phases present. Clearly, major properties such as stability to alpha-recoil damage or elemental chemical durability cannot be understood without knowing some details of the microstructure within the waste form.

Solid-state analytical work is routinely undertaken as part of most studies reported in other sections of this report. More detailed examination of thermal effects for both glasses and crystalline forms are directed toward optimizing preparation conditions, evaluating long-term self-heating effects, and defining effects in possible accident scenarios. The materials are usually evaluated over broad ranges of time (hours to years) and temperature (25° to 1400°C), both with respect to vaporization losses and to changes in the solid state. Although waste solids are very complex, most of the usual structural and element-sensitive analytical tools available have been utilized successfully. Methods include x-ray diffraction, optical and electron microscopy, bulk x-ray fluorescence analysis and electron microprobe analysis. Other specialized techniques such as alpha-radiography, Auger elemental depth profiling and transmission electron microscopy are also used in some work.

At the present time much more property information is available for nuclear waste glasses than for crystalline nuclear waste forms; this is due in part to the difficulty of analyzing micron-size crystallites in ceramics such as supercalclines. It is nevertheless known that crystalline waste forms offer more thermal/phase stability than do glasses--both with respect to vaporization losses and to changes in microstructure. On the other hand, volatility losses for glasses are also very small, and thermally induced changes (devitrification) can be avoided or controlled. A glass-ceramic waste form, as proposed by workers in Germany, can be produced by the controlled devitrification of specially formulated glasses (Lutze 1979).

The following paragraphs review some of the major features of work during the past year. Further studies will continue to provide volatility-loss comparisons between glasses and crystalline composites. For crystalline waste forms, much more information on phase concentration/compositions is needed, as are time-dependence studies of high-temperature changes. With respect to glass devitrification, work will be broadened to cover the large composition field being evaluated in glass development studies.

VOLATILITY

Volatility studies in our work rely upon thermogravimetric methods with "cold finger" collection of vaporized species (for subsequent chemical analyses). Some results have already been reported by Gray (1976). For waste glasses and for supercalclines, vaporization appears to follow an Arrhenius temperature dependence with activation energies such that volatility at 1100°C decreases a factor of 10^5 or more at $\sim 600^{\circ}\text{C}$. As expected, the alkali elements are major contributors--especially important because Cs is a major biohazard for the first few hundred years.

Results for Cs are summarized in Figure VIII.1 for several glasses, for a Purex-type calcine composition (PW-4b), and for several hot-pressed supercalcine formulations. Also, some single-point data are shown for $\text{CsAlSi}_2\text{O}_6$ and CsAlSiO_4 . It is important to recognize that the fractional losses reflect the sample size and geometry used in the experiments. A fractional loss of 10^{-2} after 4 h in this work relates only to a sample depth of ~ 1 cm. Volatility from the top of a large canister, for example, would be orders of magnitude smaller in terms of fraction lost. In a comparative sense, the results clearly show crystalline forms have volatility losses 10 to 100 times lower than do typical waste glasses. For glasses, the presence of water has a small effect, and addition of alumina reduces Cs volatility--probably by simple increase of the viscosity. It is noteworthy that unconsolidated calcine PW-4b shows high losses at 800°C . For both glasses and supercalcines, projected volatility losses at low temperatures (e.g., 500°C) are negligible.

FIGURE VIII.1 Fraction of Cesium Lost after 4 h at Respective Temperatures from a Thin (~ 1 -cm) Sample of Material

GLASS DEVITRIFICATION

Detailed devitrification studies have been made on eight glass compositions using isothermal and constant cooling rate methods. Details on glass 72-68 have been reported earlier (Turcotte and Wald 1978). More recent work on four glass compositions prepared with actual high-level waste (HLW) calcine shows that simulated glasses do show the same behavior seen in actual HLW glasses (Wald and Westsik 1979). The work on simulated and HLW glasses continues to suggest that devitrification has a relatively small effect upon mechanical and chemical durability. It also indicates that radioactivity does not affect the types of crystal phases formed.

Figure VIII.2 shows "percent-crystallinity" curves as a function of temperature for three glass compositions after annealing periods of 1 d and 60 d, as estimated by x-ray diffraction. Table VIII.1 lists the phases present in each of the glasses. The least stable glass (77-260) shows a bimodal crystallinity envelope arising from rapid formation of a gadolinium titanate phase at high temperatures, whereas formation of a rare-earth apatite phase becomes important at longer times and lower temperatures--being the major contributor to a 45% crystalline content after 60 d at 600°C. Composition 76-68, which contains high iron and sodium concentrations, is nevertheless the most devitrification-resistant glass studied--both with respect to crystal yield and to the temperature region over which significant changes occur (600°C to 800°C). However, it too becomes extensively crystallized after annealing at 650°C for one year, with a slow-forming silicate ($\text{NaFeSi}_2\text{O}_6$) becoming the predominate phase. Figure VIII.3 illustrates the devitrification kinetics in the form of time-temperature-transformation (ttt) curves for a 5% crystal yield for two of the glasses. Most of the data available for other glass compositions falls near or within the region bounded by the two curves given. It should be noted that the curves are overall representations of rather complex processes, since two to three major phases are crystallizing with different time-temperature kinetics--each with its own liquidus temperature. The relatively narrow band describing crystallization kinetics is a direct result of a glass development criterion that viscosity should be ~ 200 poise or less at 1050°C. Hence, most waste glass compositions studied to date have similar ion mobilities in the melt, giving rise to relatively narrow property ranges. If the curve for glass 76-68 is examined, it is clear that $\sim 5\%$ crystalline yield is achieved in one day (or slightly less) at between 700°C and 800°C. At 650°C, 10 d are required, and at 590°C one year is needed. At 875°C, 5% devitrification is not achieved even though the kinetics are rapid, because the glass is near the liquidus temperature ($\sim 900^\circ\text{C}$).

The effect of devitrification on leach rate is minimal, as is reported in Section VII. With respect to physical integrity, formation of large crystals has been observed to cause microcracking, which can, however, be entirely avoided by maintaining temperatures at not more than $\sim 100^\circ\text{C}$ above the dilatometric softening point. For present waste glasses, long-time annealing at temperatures between 500°C to 650°C results in a fine dispersion of micron-sized crystals similar to glass-ceramic textures. No crystallization has been observed below 500°C.

FIGURE VIII.2. Percent-Crystallinity Curves as a Function of Temperature for 1-d and 60-d Anneals

TABLE VIII.1. Principal Crystalline Phases Observed in Devitrified Waste Glasses 72-68, 76-68 and 77-260

Crystalline Phases	Waste Glass Designation		
	72-68	76-68	77-260
RuO_2	X	X	X
NiFe_2O_4	X	X	X
Pd	X	X	X
CeO_2	X	X(a)	X(a)
Zn_2SiO_4	X(a)		
SrMoO_4	X(a)		
$\text{NaFeSi}_2\text{O}_6$		X(b)	
GdTi_2O_7			X(a)
$\text{Ca}_3\text{Gd}_7[\text{SiO}_4]_5(\text{PO}_4)\text{O}_2$			X(a)

(a) Devitrification product.

(b) Appears only after a one-month anneal.

FIGURE VIII.3. Time-Temperature Transformation (5%) Curves for Waste Glasses 72-68 and 76-68

IX. RADIATION EFFECTS

R. P. Turcotte, W. E. Weber, J. W. Wald and F. P. Roberts

The effects resulting from radioactive decay processes occurring in nuclear waste solids have been under continuing study, and previous findings were reported in past annual reports (Mendel et al. 1977; Ross et al. 1978). The current studies include work on a variety of glass compositions, a glass-ceramic, and a predominately crystalline ceramic (supercalcine). Although most of the work has concentrated on use of ^{244}Cm to accelerate alpha-decay damage, some ion bombardment work is also in progress (conducted by W. Primak, Argonne National Laboratory), as are literature reviews and experimental studies related to metamict minerals (conducted by R. Ewing and R. Haaker, University of New Mexico). Studies are also progressing toward evaluating the importance of transmutation (the specific reaction chosen for study is $\text{Cs} \rightarrow \text{Ba}$) on properties of several glass and crystalline compositions.

The work covered in the following sections shows that radiation-induced changes are not as great in glasses as in crystalline materials. Since high-energy particles induce randomness, crystals are often subject to amorphization, with corresponding large volume changes (~ 1 to 15%). Although theoretical understanding of radiation damage in glass and ceramic materials is not well developed, the damage caused by decay of the actinides can be estimated to saturate at near 10^{19} alpha-events/ cm^3 in homogeneous solids (Weber et al. 1979). In studies of waste solids, saturation effects are actually observed at doses below this estimate--often in the range 2 to 5 $\times 10^{18}$ alpha-events/ cm^3 . Doses at this level will be reached even in relatively low-activity defense wastes. Although we have demonstrated that no significant change in leach rate occurs in glasses and partially crystallized glasses due to alpha-decay (Weber et al. 1979), additional work is needed on new glass compositions, as well as on crystalline solids.

GLASSES

Glass studies have now shown that saturation of radiation effects does occur and that there is no important physical or chemical degradation, provided the actinides are homogeneously incorporated. Figure IX.1 shows the volumetric changes measured in several glasses, a glass-

FIGURE IX.1. Change in Density of Waste Materials as a Function of Alpha-Radiation Dose

ceramic and a supercalcine; these changes are small in all cases, and can be near zero for glasses, depending upon the composition. There is a possibility that physical integrity may not be retained if the actinides are inhomogeneously concentrated at certain locations in the glass, because of glass-glass phase separation or through formation of insoluble oxides or devitrification products. Such segregations may lead to inhomogeneous volumetric changes not easily accommodated in brittle materials. Several experiments have been completed which, in fact, demonstrate that devitrified glasses with large crystal size (210 μm) can be microfractured by nonhomogeneous radiation damage. Even in dilute concentration (i.e., ~ 0.05 wt%) the actinides readily crystallize, and also directly follow glass-glass phase separation if it occurs.

To examine the behavior of dilute concentrations of actinides, three glass compositions (77-260, 77-107, and SRP-1) were doped with actinides at levels as follows (in wt%): $^{237}\text{Np}(0.25)$, $^{239}\text{Pu}(0.04)$, $^{243}\text{Am}(0.04)$, $^{244}\text{Cm}(0.015)$. Glasses were prepared by adding nitric/HF acid solutions of the individual actinides to the powdered simulated waste glass and then melting at 1050°C for 4 hours. Heat-treatment followed, with 96-h anneals being done at 950°C or 850°C . In all cases, a marked tendency to crystallize was observed, generally with Np and Pu behaving in a similar fashion (i.e., M^{4+}) and Cm and Am following the same trends (i.e., M^{3+}). An alpha-autoradiograph obtained using the cellulose-nitrate method is shown in Figure IX.2 for Am, following treatment at 850°C for glass SRP-1. The lower-temperature treatment produces relatively large needle-shaped rare-earth aluminum-silicate crystals, as well as a second phase concentrating near the surface of the melt. Following the 950°C treatment, two of the three glasses showed some evidence of macro-scale glass-glass phase separation, with a corresponding inhomogeneous distribution of the actinides. We would postulate that if such actinide phase separation occurred in an actual high-level waste glass, the radiation-induced volume changes would also be inhomogeneous, leading to micro-cracking. Experimentally, strength loss (cracking) has never been observed in any of our radiation damage studies of as-melted glasses, although there has been one report of radiation-induced cracking by Bibler and Kelley (1978).

We have recently completed a radiation damage study which involved the intentional crystallization of glass. In this work, glass 77-260 was doped with ^{244}Cm (2 wt%). Separate portions were heat-treated so that one had a microstructure with a uniform dispersion of small crystals and the other had a coarse distribution of larger crystals. From previous work, we knew that a major devitrification phase in this glass was a rare-earth silicate (apatite), which was susceptible to amorphization. The micrographs given in Figure IX.3 show the as-prepared glass (a), a large crystal sample (b), and a small crystal sample (c). The alpha-radiograph (d, e) shows that the Cm is highly concentrated in two crystalline phases: a rare-earth silicate and a rare-earth titanate. Even before radiation effects had caused the silicate phase to become fully x-ray-amorphous, rather extensive microcracking was observed (Figure IX.3f). Other details of the work, including results of density, stored energy, impact and leaching tests have been reported (Weber et al. 1979). Major conclusions from the study are:

FIGURE IX.2. Alpha-Radiograph Showing Concentration of Am Dopant (0.04 wt%) in Devitrification Phases

- Physical/structural changes in the devitrified glasses are greater than those seen in the vitreous form. Nevertheless, radiation-induced changes in density, leachability, impact behavior and stored energy are small in all cases.
- In this study, the gadolinium-titanate phase with a cubic structure was stable to self-radiation. The apatite structure $[\text{Ca}_3\text{Gd}_7(\text{SiO}_4)_5(\text{PO}_4)_2\text{O}_2]$ was unstable and transformed to an x-ray-amorphous state. There is a relatively large radiation-induced increase in crystal volume, causing microfracturing of the glass matrix. The cracking is minimal if the crystals are small ($<5\ \mu\text{m}$).
- For the glass compositions studied, self-radiation does not significantly affect chemical durability or impact performance. Neither the observed crystalline phase amorphization nor the microfracturing cause major changes in the net material leached or in the impact particle size distribution.

FIGURE IX.3. Initial Microstructures in the Three Waste Glass Forms Investigated and Alpha-Autoradiograph with Corresponding Optical Images Before and After Micro-Fracturing(a)

(a) As-prepared, vitreous sample (a); partially devitrified sample cooled at -60°C/h (b); partially devitrified sample annealed at 700°C for one week (c); alpha-autoradiograph of region shown in (e) and (f), (d); slow-cooled sample (-60°C/h) exhibiting no microcracks after 2×10^{16} α -decays/ cm^3 (e); microcracks developed in same area after 8×10^{17} α -decays/ cm^3 (f).

CRYSTALLINE WASTE SOLIDS

The greatest radiation damage effects observed in glass systems result from the presence of crystalline phases that are susceptible to alpha-recoil damage. Studies are just beginning that will quantify the significance of amorphization of crystalline phases with respect to changes in chemical durability. It has been pointed out by Ewing and Haaker (1979) that in nature, metamict zircon is more highly altered than are adjacent layers of undamaged zircon, but that the chemical changes are poorly understood.

To ensure continued physical integrity, it would seem that large volume changes of any individual phase should be avoided. In the two crystalline waste forms studied so far, neither supercalcine nor a glass-ceramic became visibly degraded (strength tests have not yet been made), even though phases containing curium became x-ray-amorphous and exhibited relatively large volume changes. Figure IX.4 shows volume changes measured for a number of individual phases. All of the compounds shown become x-ray-amorphous in relatively short times except for PuO_2 , which only shows a moderate volume change even after receiving doses much larger than those plotted here. The apatite and titanate curves shown can be compared to the density changes measured for the parent waste form given in Figure IX.1, for supercalcine, and for the glass-ceramic. When this is done, the total waste form volume changes are larger than can be accounted for based simply on amorphization of any single phase. The reason for this is that the actinide-containing phases are point sources of 5 MeV alpha particles, which are capable of damaging adjacent material. Since the crystals are in the micron or submicron range, and since the alpha-particle range is ~ 20 microns, all of the phases present are subject to long-term radiation damage.

Although radiation damage in polyphase waste ceramics is a complex process, the net effects do not appear to be of major consequence. Much more work is required, particularly with respect to radiation-induced changes in chemical durability, and in determining effects on large-grain-sized materials.

FIGURE IX.4. Volume Changes for Crystalline Phases as a Function of Accumulated α -Damage

X. THERMAL AND MECHANICAL SHOCK

L. R. Bunneil

As part of an effort to characterize the effect of impact on large (up to 0.91-m-dia) canisters filled with simulated Hanford waste glass by the ceramic melter, canisters were first examined in the as-filled condition. Canisters of three different diameters were examined:

Canister 32 = 0.41 m in dia x 2.74 m long;

Canister 31 = 0.61 m in dia x 2.43 m long;

Canister 36 = 0.91 m in dia x 2.74 m long.

The glass in the canisters was made available for examination by removing full-length, 120° sectors of the walls using a milling machine. The sections were lifted away and the contents of each canister were examined visually. Canister 32, shown in Figure X.1, is representative. In all cases, the glass immediately adjacent to the canister was severely thermally quenched and had separated into concentric layers 0.16 to 0.64 cm thick. The glass showed a number of complex flow patterns--a result of the fill rate (~45 kg/h) and the quench caused by pouring the glass into a room-temperature canister. Because of the outer-layer cracking, the outer 2.5 cm was sampled separately. The glass pieces became larger as the core of the canister was approached; pieces nearly 15 cm in dia were found at the center. Since the larger fragments were locked into place, all sizing data is somewhat biased toward smaller sizes because of the physical force necessary to dislodge the samples.

After the glass was hand-sorted into +7.6-cm and -7.6-cm fractions, it was sieved. A shaker, a set of standard sieves and a 1-h shaking time were used. The sieving also generated fines not in the original sample. Table X.1 shows the sieving results to a minimum screen size of 44 μm . The fraction passing that screen size, including the -10- μm material generally regarded as respirable, was evaluated by a sedimentation technique.^(a) The respirable fraction is extremely small ($<2.7 \times 10^{-3}\%$) for canister 31.

Specific surface areas for the glass were calculated by assuming that the particles were spherical. The area was 0.63 cm^2/g for the 0.41-m can, 0.91 cm^2/g for the 0.61-m can, and 0.56 cm^2/g for the 0.91-m can. This surface area is a factor of considerable interest, since it can be used to calculate the ratio of surface area, including cracks, to that of an uncracked monolith of the same dimensions. The ratio was 18.1:1 for the 0.41-m can, 27.4:1 for the 0.61-m can, and 33.9:1 for the 0.91-m can. The increasing ratios result from the relative constancy of the specific surface area combined with the lower surface/volume ratio that accompanies an increase in can sizes. The ratio of surface to volume can be related to a radius for a sphere. At a value of 0.63 cm^2/g (0.41-m can) the equivalent radius is 1.6 cm, indicating that all of the waste glass in the canister was reduced by cracking to the equivalent of ~3-cm-dia spheres.

(a) Sedigraph 5000, Micromeritics Corporation.

FIGURE X.1. Canister CM-1, with Sector Removed from Side^(a)

(a) Note flow patterns--most evident near the canister bottom, where glass contacted coldest metal.

TABLE X.1. Sizing Data (+44 μ m) for As-Filled Canisters

Sampling Location	Screen Size, mm ^(a)								
	150	72.6	25.4	2.83	0.850	0.420	0.150	0.074	0.044
#32 0-30 cm from bottom, 0-2.5 cm in	100	100	24.3	1.38	3.18×10^{-1}	1.63×10^{-1}	5.94×10^{-2}	2.76×10^{-2}	1.27×10^{-2}
#32 0-30 cm from bottom, 2.5 cm to center	100	69.6	9.02	6.67×10^{-1}	1.39×10^{-1}	7.97×10^{-2}	2.72×10^{-2}	1.27×10^{-2}	7.30×10^{-3}
#32 1.2-1.5 m from bottom, 0-2.5 cm in	100	87.1	19.0	1.64×10^{-1}	4.86×10^{-2}	2.60×10^{-2}	8.22×10^{-3}	2.80×10^{-3}	1.08×10^{-3}
#32 1.2-1.5 m from bottom, 2.5 cm to center	100	46.7	8.91×10^{-1}	3.50×10^{-1}	8.06×10^{-2}	4.24×10^{-2}	1.47×10^{-2}	6.64×10^{-3}	3.62×10^{-3}
#32 Top 0-2.5 cm in	100	77.5	12.4	1.82	3.64×10^{-1}	1.94×10^{-1}	8.08×10^{-2}	3.95×10^{-2}	2.65×10^{-2}
#32 Top, 2.5 cm to center	100	32.3	4.21	2.96×10^{-1}	5.39×10^{-2}	2.55×10^{-2}	8.20×10^{-3}	3.51×10^{-3}	1.97×10^{-3}
#31 Bottom 0-2.5 cm in	100	100	17.5	1.94	1.01	2.00×10^{-1}	8.91×10^{-2}	2.64×10^{-2}	1.04×10^{-2}
#31 Middle 0-2.5 cm in	100	80.0	12.8	7.55×10^{-1}	2.08×10^{-1}	1.15×10^{-1}	5.67×10^{-2}	3.14×10^{-2}	2.14×10^{-2}
#31 Top 0-2.5 cm in	100	92.0	8.72	5.57×10^{-1}	1.62×10^{-2}	9.43×10^{-2}	4.09×10^{-2}	2.18×10^{-2}	1.34×10^{-2}
#6 Impact area			100	45.8	20.98	12.14	4.53	2.27	1.32
#36 Bottom 0-2.5 cm in	100	68	11	3.24×10^{-1}	1.42×10^{-1}	9.22×10^{-2}	2.21×10^{-2}	8.30×10^{-3}	3.86×10^{-3}
#36 Bottom 2.5 cm to center	100	89.2	21	1.12	3.17×10^{-1}	1.70×10^{-1}	3.23×10^{-2}	1.45×10^{-2}	6.30×10^{-3}
#36 Middle 0-2.5 cm in	100	85.3	8.70×10^{-1}	5.01×10^{-1}	1.3×10^{-1}	7.5×10^{-2}	1.88×10^{-2}	7.58×10^{-3}	4.12×10^{-3}
#36 Middle 2.5 cm to center	100	36.4	1.44	1.06×10^{-1}	3.45×10^{-2}	2.07×10^{-2}	7.22×10^{-3}	3.23×10^{-3}	1.78×10^{-3}
#36 Top 0-2.5 cm in	100	62.4	5.65	1.51×10^{-1}	3.28×10^{-2}	1.78×10^{-2}	5.86×10^{-3}	2.29×10^{-3}	1.15×10^{-3}
#36 Top 2.5 cm to center	100	32.1	2.05	9.46×10^{-2}	3.53×10^{-2}	2.43×10^{-2}	1.51×10^{-2}	1.24×10^{-2}	8.11×10^{-4}

(a) Weight percentages finer than stated screen size.

Examination of the as-filled canisters prompted the recommendation that the canisters be heated during filling. This was accomplished by insulating the cans during pouring, which resulted in noticeable improvements in quality as noted from external examination of the glass. Quantitative evaluation of fracturing in one of these insulated canisters has not yet been done.

The increase in surface area of glass in a canister subjected to a severe impact was also determined. Canister #6 (an as-filled canister 0.4 m in dia with a 0.6-cm carbon-steel wall and a hemispherical bottom) was dropped 7.62 meters. The canister was sampled in the zone of maximum impact. Sizing was done on the material from the impact zone and is compared in Figure X.2 with the as-filled 0.61-m canister. The log-log scales are used only to cover the ranges of interest; no exponential relationship is necessarily implied. The calculated surface area of the material was $24.3 \text{ cm}^2/\text{g}$ after impact. Sedimentation size analysis showed that the $-10\text{-}\mu\text{m}$ fraction was increased to 0.13% by impact (1.3% at $-44 \mu\text{m}$ x 10% at $-10 \mu\text{m}$). The severely impacted zone extends only $\sim 0.5 \text{ m}$ from the impact point, and the rest of the glass in the canister appears to have suffered only minimal damage.

FIGURE X.2. Sieve Analysis Data for Two 0.61-m Canisters--One As-Poured and One After Impact Testing^(a)

^(a) Note log scales.

XI. QUALITY VERIFICATION

W. L. Kuhn, L. M. Browne, Y. B. Katayama, J. M. Lukacs

This section addresses the characterization of "engineering-scale" glasses produced during vitrification equipment development and demonstration runs. The ultimate goal of quality verification is to document the reproducible and predictable aspects of homogeneous waste packaging. To this end, characterization methods are evolving to report quantitative data as a function of location in glass canisters that are suitable for constructing a data base amenable to statistical analyses and comparisons to process expectations.

Notable activities this year included characterization of products from continuous demonstration runs, evaluation of glass behavior in full-scale equipment, and continued evaluation of glass produced during the Waste Solidification Engineering Prototypes (WSEP) Program.

SRP CERAMIC MELTER DEVELOPMENT RUNS

A series of eight ceramic melter runs with simulated Savannah River waste were conducted to evaluate glass processing. About 6000 kg of glass was produced, filling four 0.61-m-dia by 2.90-m-long canisters. Figure XI.1 illustrates the variation of the process variables (melter electrode temperature and fill rate) and the product variables (densities and leach rates--Soxhlet method, 72 h at 99°C) for the fourth through seventh runs. Glass from the four runs was all collected in canister number 52. The density of the glass in canister 52 was practically constant; variability in the leach rate is thought to be within the precision of the Soxhlet method, with no correlation to process variations being found.

Optical examination of polished sections of cores taken from Canister #52 reveals varying concentrations of finely divided crystals, as shown in Figures XI.2, XI.3, XI.4, and XI.5, corresponding to the 15-cm, 61-cm, 121-cm, and 152-cm fill levels in the canister. No correlation between leach rate and crystal concentration was detected.

SRP IN-CAN MELTER DEVELOPMENT RUNS

Pilot-scale ICM runs were conducted to evaluate the melting characteristics of Savannah River frit/calcline mixtures. During run SRP-ICM-7 we put the furnace through a slow cool-down: 1050°C to 755°C over 5.7 h, followed by an 11.5-h hold at 755°C. Previous experience with PNL glass compositions under such cooling has been satisfactory; however, the SRP glass (Frit 411, Composite SRP waste at 3:1) devitrified extensively.

Examination of SRP-ICM-7 glass samples revealed the presence of lithium-metasilicate (Li_2SiO_3) at about 32 wt%, plus an unidentified lesser phase. Microcracking was extensive. Subsequent laboratory remelts and anneals verified devitrification at 750°C; at 1000°C no crystallization occurred. Soxhlet leach rates (72 h at 100°C) for samples from SRP-ICM-7 were 1.2 to 1.5×10^{-4} g/cm²-d--which is about 70% greater than for previous, similar SRP-ICM pilot-scale runs, during which there was no hold at 750°C.

FIGURE XI.1 Process and Product Variables for Canister #52, Which Was Filled in Runs SRP-4 through SRP-7

FIGURE XI.2. Micrograph of Glass Sample from Canister #52
15 cm Above Bottom

FIGURE XI.3. Micrograph of Glass Sample from Canister #52
61 cm Above Bottom

FIGURE XI.4. Micrograph of Glass Sample from Canister #52
122 cm Above Bottom

FIGURE XI.5. Micrograph of Glass Sample from Canister #52
152 cm Above Bottom

A full-scale (61-cm-dia can) in-can melt of Savannah River glass was conducted to evaluate the resulting product. Product characterization is summarized in Tables XI.1 and XI.2. Table XI.2 is obtained from x-ray-fluorescence analyses of several transition metal elements; the concentrations were obtained as ratios of x-ray-fluorescence intensities with silicon intensity as a standard. Since a calibration for the glass samples has not been developed, the fluorescence ratios cannot be directly converted to atom-percent composition. Instead, the average ratio over the five samples is calculated for each element (see last row in Table XI.2) and used to normalize the fluorescence ratios for the various samples. The relative variation in concentration over the samples is thereby presented for each element.

X-ray-diffraction analysis confirms that roughly half of the crystalline material in Sample 1 is spinel; the remainder is not yet identified. The accumulation at the bottom indicates the settling of heavy crystallites (devitrification products or insolubles). Note that the Soxhlet leach rates do not correlate well with percent-crystallinity values.

WSEP GLASS CHARACTERIZATION

The leach rate of radioactive, simulated HLW borosilicate glass produced during run SS-12 of the WSEP Program has been reported previously after 8 mo (Mendel and McElroy 1972) and 2.8 yr (Mendel 1973) of storage. Additional samples were recently core-drilled from SS-12

TABLE XI.1. Product Characterization for SRP-ICM Run with 61-cm Can

Sample No.	Location, cm above bottom	Density, g/cm ²	Soxhlet Leach Rate, g/cm ² -d	Crystallinity, vol%
1	0 to 33 on center	2.75	1.6×10^{-4}	46
2	30 at outer surface	2.64	2.2×10^{-4}	8
3	63 at outer surface	2.64	8.6×10^{-5}	2 to 3
4	109 at outer surface	2.62	1.6×10^{-4}	2 to 3
5	155 at outer surface	2.64	9.7×10^{-5}	2 to 3

TABLE XI.2. Chemical Analyses for SRP-ICM Run with 61-cm Can

Element Sample No.	Relative Concentrations				
	Fe	Al	Cr	Mn	Ni
1	1.79	2.01	1.68	1.82	1.57
2	0.87	0.76	1.01	0.80	0.71
3	0.72	0.71	0.72	0.78	0.97
4	0.73	0.79	0.64	0.77	0.99
5	0.89	0.72	0.96	0.83	0.76
Unnormalized Average Ratio Compared to Si	8.278	0.139 ^(a)	0.377	1.419	0.708

(a) Ti secondary target; all others are for Ba secondary target.

after 8.4-yr storage, 3 yr of which was at temperatures of 400⁰ to 450⁰C. Radiation exposure during the storage period is estimated to be 2.2×10^{11} rads/g. Leach tests were conducted in a Paige extractor at 25⁰C with deionized water.

The results of the leach tests based on Cs¹³⁷ are compared in Figure XI.6 to the 8-mo and 2.8-yr results. Through 175 d of leaching, no significant changes from the 8-mo-old glass data are seen, which demonstrates significant stability of glass castings in thermal and radiation environments.

FIGURE XI.6. Leach Rate Based on ¹³⁷Cs Release of Borosilicate Glass Vitrified During WSEP Run SS-12 After Storage Periods Indicated

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APPENDIX
REPOSITORY CONSEQUENCE ANALYSES

APPENDIX

REPOSITORY CONSEQUENCE ANALYSES

A methodology has been developed for analyzing the potential radiologic dose consequences from deep geologic repositories that would result from a scenario involving groundwater penetration into a repository, leaching of the radionuclides from the waste, and transport of the nuclides to the biosphere, where they may interact with humans (Burkholder et al. 1975). This methodology is now being applied in two Office of Nuclear Waste Isolation (ONWI) programs. The Systems Study on Engineered Barriers Program application will provide a perspective on what benefit may be obtained by reduced leach rates, more durable containers, or increased sorption of nuclide ions. This benefit is measured in terms of incremental dose reduction achieved by barrier improvement. The Ore Bodies Comparison Program application involves applying the same methodology to naturally occurring uranium ore deposits in order to determine the potential dose consequences from ore deposits relative to those from a man-made repository.

SYSTEMS STUDY ON ENGINEERED BARRIERS

The development and characterization of waste forms, containers and other engineered barriers destined for use in the isolation of nuclear waste in deep geologic repositories has progressed to the point where there are several options and combinations of barrier systems that are available to help assure safe disposal of nuclear wastes. However, a rigorous basis has not yet been developed to select materials or to define required characteristics. This analysis is an attempt to develop an initial perspective on what is needed in order to establish that basis. The intent of the analysis is to roughly determine what incentives exist for providing highly durable engineered barriers for the isolation of radioactive waste in a deep geologic repository, based on what effect, if any, the engineered barrier may have on the ultimate potential dose to humans.

The highest risk path from the storage site through the geosphere to the biosphere is assumed to be the "leach incident pathway."^(a) The geologic isolation system ideally provides barriers to the process by two general means: 1) containment of the waste for a length of time sufficient to allow the hazardous nuclides to decay to innocuous levels, such that unrestricted release to the environment presents no unacceptable radiological hazard; or 2) limiting the rate of nuclide release to the biosphere so that nuclide concentrations in the constantly renewed local surface water and air never exceed acceptable limits.

(a) To this point in the analysis, the "leach incident pathway" has been assumed to be the highest risk pathway. However, a human intrusion event such as a waste well penetration near the repository may be the limiting scenario and is being investigated at this writing.

The actual repository system will provide protection by using some effective balance of these two means. The available system components that provide these means for protection can be reduced to: 1) the waste form, 2) the containment package, and 3) the geology (including hydrology).

The radionuclide inventory used in the analysis is one-fifth of the total for the spent, unprocessed fuel (no-recycle case) accumulated in the U.S. through the year 2050 that was used in the Draft Commercial Waste Management Generic Environmental Impact Analysis (DOE/EIS-0046-D) (1979). The assumption was that there would be five operating repositories, each containing an equal fraction of the total U.S. spent-fuel accumulation.

The geosphere transport model simulates the release of radionuclides from a repository through contact and leaching by flowing groundwater, through subsequent transport of the nuclides in the groundwater (including the effects of convection, sorption, and radioactive decay), and through ultimate release of the nuclides to the surface water (lake or river). In order to simplify the analysis, a multitude of parameters were reduced to terms representing the net effect of several more complex phenomena.

The release rate of nuclides into the flowing groundwater (source term) is a constant rate approximation (%/yr) of what may in reality be a more complex release function that can be more explicitly modeled after in-situ performance analyses have progressed sufficiently. A parameter representing the combined durability of the engineered barrier containment function and the stability (or integrity) of the surrounding geology is the delay (years) in release-incident initiation, measured from the date of repository closure. The major hydrologic parameters are dispersivity, groundwater flow rates, and total pathlength to the biosphere. These are functions of geologic media factors such as porosity, permeability, net hydraulic head, and gradient and fracture patterns. For this analysis, these parameters have been reduced to groundwater travel time (pathlength/flow velocity) and a net dispersion coefficient. Output data of the geosphere model is the input data for the biosphere model. The biosphere model (Denham et al. 1973; Soldat, Robinson and Baker 1974; Baker, Hoenes and Soldat 1975) predicts the radiation dose to humans from the nuclide release to surface waters via several pathways--including direct ingestion of water, aquatic foods and irrigated food products, as well as irradiation from shoreline deposition and swimming. Food chain reconcentration/accumulation effects are included.

The methodology was applied to one generic site and, to a limited extent, to a more realistic reference site utilizing measured and estimated parameters. The parameters for the generic site were chosen to maximize any incentive for providing a long-lived container or other means of delaying groundwater contact with and leaching from the waste matrix. Sorption properties of the surrounding geologic media were taken from BNWL-1927 (Burkholder et al. 1975). The results of the generic analysis are summarized in Figure A.1. Note that delaying the release initiation for up to 10^6 yr has no effect upon the potential dose even for very short groundwater travel times of 10 and 100 years. This is because the dose-controlling nuclide is ^{226}Ra generated by decay from the very long-lived ^{238}U and ^{234}U . The groundwater travel times shown in Figure A.1 are much shorter than would reasonably be expected for any

FIGURE A.1. Potential Maximum Dose Rate Versus Delay in Release Initiation for Generic Site

site that would be selected as a repository; they were chosen as parameters in order to determine how small this parameter would have to be in order to observe any effect due to the delay in release-event initiation. The relative difference in resultant dose predicted for the 10-yr and 100-yr groundwater travel times in Figure A.1 is the result of a much greater time and distance dispersion of the ^{226}Ra daughter product in the 100-yr case, which is in turn caused by the large sorption differences among members of the decay chain.

Figure A.2 shows the effect of the release rate on the potential dose from the generic site with a groundwater travel time of 100 yr after a release-initiation delay of 10^6 years. The graph in Figure A.2 indicates that even after a delay of one million years, the release rate of nuclides from the waste matrix into the groundwater has a significant effect upon the potential dose from the scenario. The dose-controlling nuclide for short-release durations (fast release), ^{129}I , is rapidly reduced in dose contribution with decreasing release rate until it ceases to dominate the potential dose at a release duration of about 20 years. The dashed line in Figure A.2 indicates the continuing ^{121}I potential dose trend. The release rate is seen to have almost no effect upon the potential dose from the ^{226}Ra until the release duration exceeds 10^5 years. After this point, the ^{226}Ra dose potential decreases rapidly. This behavior is typical of what has been observed (from modeling) for the transport of nuclides that are the products of complex decay chains. The different sorption properties of the members of the decay chain disperse the members greatly during transport, and the duration of the release into the groundwater has little effect on the ultimate release of decay products until the release duration approaches the order of magnitude of the sorption distribution (in years) of all members of the chain.

This effect may also be observed in some limited results from the reference site analysis. The groundwater travel time for the reference site (40,000 yr) and site sorption

FIGURE A.2. Potential Maximum Dose Rate Versus Release Rate for Generic Site

characteristics are much more realistic than are those for the generic site, and are probably closer to those that would be representative of a site considered for a repository. The graph in Figure A.3 indicates a nearly linear reduction in the ^{129}I potential dose with decreasing release rate (absolute linearity would exist if the effects of dispersion were not considered). This is because the iodine is not a product of decay chains and, even on the time scale of Figure A.3, has an essentially infinite half-life. The ^{226}Ra , however, is the product of the decay chain $^{238}\text{U} \rightarrow (^{234}\text{Th} \rightarrow ^{234}\text{Pa}) \rightarrow ^{234}\text{U} \rightarrow ^{230}\text{Th} \rightarrow ^{226}\text{Ra}$, and the release duration has very little effect upon the potential ^{226}Ra dose until it exceeds 10^5 years.

For the sites analyzed, the graphs in Figures A.2 and A.3 suggest that after a maximum, sustained-release rate equivalent of less than $1.0\%/yr$ is attained, very little benefit is realized until the release rate is reduced further--to less than $10^{-3}\%/yr$. This lower rate would be equivalent to a right-cylindrical waste form with a density of $3 \text{ g}/\text{cm}^3$, a diameter of 0.3 m , and a simple corrosion-model net leach rate of $10^{-6} \text{ g}/\text{cm}^2\text{-d}$. For a spherical particle diameter of 1 cm , the equivalent leach rate would be about $4 \times 10^{-8} \text{ g}/\text{cm}^2\text{-d}$. The above are observations based on very limited results and are not considered to be conclusions. More conclusive results will be available later in this effort, after the methodology is applied to fairly well defined reference sites. All quantitative values presented here are intended for methodology illustration only, and should not be put to any other use.

FIGURE A.3. Potential Maximum Dose Rate Versus Release Rate for a Reference Salt Site

ORE BODIES COMPARISON

It has been suggested that one general criterion for deep geologic repositories containing spent fuel is that they should represent no greater radiological risk than that posed by naturally occurring uranium ore deposits. While the tools for performing a classic risk analysis on a geologic repository or an ore deposit are not yet available, a methodology has been developed for estimating the potential radiologic consequences resulting from groundwater intrusion, leaching, and nuclide transport scenarios (Burkholder et al. 1975). This methodology has been applied in a very limited manner to predict the potential radioactive release from ore bodies in order to compare these calculations with those performed in the past for spent-fuel repositories (GEIS). As a check on the ore bodies release estimates, the calculated results from the ore bodies analysis have been compared to actual measured surface-water concentrations of radioactive material that apparently had its origin in natural ore bodies.

Descriptive data for two major ore deposits were gathered from available literature and from discussions with United States Geological Survey experts in Grand Junction, Colorado. Potential dose consequences from these ore bodies were then calculated using the same methodology as was applied in limited analyses of spent-fuel repositories. The two ore deposits are

Granite Mountain, Wyoming and the Rossing deposit in South West Africa. These two sites were picked because of their large uranium inventories. The Granite Mountain deposit is a widely distributed deposit, and has a lower specific uranium concentration than does the Rossing deposit, which is more compact. The characteristics of the Granite Mountain deposit are assumed to be those present nearly 60 million years ago. It has been determined that some granite samples from the Granite Mountain region have lost nearly 80% of the uranium originally contained in them--this uranium having been leached away during the last 60 million years. The Rossing deposit of South West Africa was chosen because of its high specific activity: between 30 and 130 times that of Granite Mountain. The deposit is in the very dry Namib Desert. The annual rainfall there is about an inch per year. The deposit is near the edge of the Khan River Basin, but the river contains water only when there is runoff from the infrequent rains. Thus, the leaching of uranium from the deposit is slow. Pertinent data regarding these two deposits and the reference repository are summarized in Tables A.1 and A.2.

Data was also obtained from uranium concentrations in surface streams in order to evaluate whether actual releases from natural deposits provide potentially high dose consequences. Fix (1956) listed several of these values; the highest small-stream value reported was 32 ppb in Bishop Creek, Montana, and the highest river concentration was 4 ppb in the Sevier River in Utah. It may be significant that various types of mining operations had been initiated in the general area of these streams before these data were collected. These values served as input for the biosphere model to estimate the potential dose consequences resulting from these surface concentrations.

TABLE A.1. Nuclide Inventories for Ore Bodies and Reference Repository

Nuclide	Initial Inventories, Curies		
	Reference Repository	Granite Mountain	Rossing Deposit
^{238}U	2.4E4	3.4E7	1.9E5
^{234}U	1.3E5 ^(a)	3.4E7	1.9E5
^{230}Th	2.9E1	3.4E7	1.9E5
^{226}Ra	2.9E-1	3.4E7	1.9E5
^{129}I	2.5E3	--	--

(a) Includes ingrowth from ^{238}Pu during first 1000 years.

TABLE A.2. System Parameters for Ore Bodies and Reference Repository

Site	Groundwater Velocity, m/yr	Migration Pathlength, km	Groundwater Travel Time, yr	Leach Rate, fraction/yr
Reference Repository	1.3E0	5.6E1	4.3E4	4.0E-3 - 1.0E-6
Granite Mtn.	2.2E-1	1.0E1 - 3.2E1	4.5E4- 1.5E5	1.3E-7 - 1.3E-8
Rossing	1.1E0	3.2E0	3.0E3	1.0E-7

The potential annual maximum-individual dose for the repository and the two reference ore bodies as well as for selected surface waters are summarized in Figure A.4. The peak releases in all cases occur over such long periods of time (thousands to millions of years) that they can be considered as chronic, constant environmental conditions.

The calculated potential dose to a maximum individual from the generic repository ranges from a high of about 700 mrem/yr to a low of about 80 mrem/yr for the range of parameters used. This compares with a range of 1200 to 120 mrem/yr calculated dose from the Granite Mountain deposit and a single calculation of 5 mrem/yr from the Rossing deposit. The potential dose to the maximum individual calculated for the surface waters was based on the assumption that ^{226}Ra was in decay equilibrium with the reported uranium concentrations in the streams. The calculated potential dose to the maximum individual for the various streams were:

- Bishop Creek = 30,000 mrem/yr;
- Sevier River = 4000 mrem/yr;
- average Wyoming surface water = 600 mrem/yr.

The per-capita general population dose from the Wyoming average surface-water concentrations would be in the range of 100 to 200 mrem/yr.

Based only upon these limited calculations, it appears from the standpoint of potential radiological consequences that the spent-fuel repository and the large bodies are quite comparable. In fact, apparent releases from some ore deposits (based upon measured uranium concentration in surface streams) probably exceed what would be considered "acceptable" releases from a man-made repository.

FIGURE A.4. Summary of Potential Radiological Consequence Results

It should be noted, however, that the limited work to date in no way forms a rigorous basis for any criteria that relate spent-fuel repository requirements to naturally occurring uranium ore bodies.

It is also worth noting that the calculated releases from the Granite Mountain deposit span the measured average value of nuclide concentrations in Wyoming surface waters (Figure A.4).

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