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Ceramic & Glass Radioactive Waste Forms

January 4-5, 1977

**Summary of a Workshop Held
at ERDA - Germantown**



Energy Research & Development Administration
Division of Physical Research & Division of Waste Management,
Production & Reprocessing

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Ceramic & Glass Radioactive Waste Forms

January 4-5, 1977

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Energy Research & Development Administration
Division of Physical Research & Division of Waste Management,
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SUMMARY

This report contains individual presentations and group reports on the subject of glass and polycrystalline ceramic radioactive waste forms. A workshop was held January 4-5, 1977 at ERDA-Germantown, Maryland and this report is a summary of that meeting. The purpose of the workshop was two-fold. First, it provided an opportunity for participants familiar with the behavior of glass and crystalline ceramics to collectively examine the important problems associated with their use as radioactive waste forms. Second, the workshop provided an improved fundamental understanding of the behavior of glass and crystalline ceramics important to long-term confinement of radioactive wastes.

The behavior of glass and crystalline ceramics as a host for radioactive waste is complex and dependent on several material and environmental parameters. There was a general consensus that the amount of information available on glass as a waste form provided a good basis for planning on the use of glass as an initial waste form. It was also the consensus that crystalline ceramic forms could also be good waste forms if much more development work were completed. It was the consensus that prediction of the chemical and physical stability of the waste form far into the future would be much improved if the basic synergistic effects of low temperature, radiation and long times were better understood. Although current information does not indicate any significant advantage for crystallized ceramics, continuing development of the polycrystalline ceramic forms was recommended. It was concluded that the leach rate of radioactive species from the waste form is an important criterion for evaluating its suitability, particularly for the time period before solidified waste is permanently placed in the geologic isolation of a Federal repository.

INTRODUCTION

With the potential increased use of nuclear power and the associated reprocessing of fuel in the future, the disposal of radioactive will become an increasingly important consideration. Since the result of reprocessing is a high-level liquid waste which can be calcined to oxides, the incorporation of the oxides with dense polycrystalline ceramics or glasses immediately come to mind as potential hosts for radioactive waste. Indeed, at the present time, the major waste host development programs are oriented toward exploiting the relative inertness of glass and ceramics as waste forms. This fulfills the requirement to have a chemically, thermally and radiolytically stable solid form for near term handling and storage of waste and to have as well a material with an attractive potential for long term stability during geologic isolation of wastes.

There are, however, some unique characteristics of waste form materials such as the internally-generated thermal and radiation conditions which are not normally encountered in the application of ceramic materials. Furthermore, it would be helpful to be able to predict the chemical and physical stability of the waste form and its interaction with various environmental factors, such as ground water, for times as long as centuries. Recognizing the importance of radioactive waste disposal and the potential role that glass and ceramic waste forms can play, the Division of Physical Research and Division of Waste Management, Production, and Reprocessing of ERDA, scheduled a workshop on the subject. The primary goals for the workshop were to familiarize those in the ceramics community with the development of glass and crystalline ceramics as waste forms, and to have them assess the present understanding of the fundamental behavior of these materials relevant to their potential use as waste forms. Experts on the behavior of glass and ceramics from universities, national laboratories, and industrial laboratories interested in radioactive wastes were invited to attend. The meeting was held on January 4-5, 1977, at ERDA-Germantown, Maryland.

This report summarizes the meeting and is organized into three parts:

I. Waste Forms

This section primarily contains presentations by various individuals actively investigating the behavior of crystalline ceramics and glass for waste hosts. The goals of these presentations are: to outline the requirements for a radioactive waste form, to present the state of waste form evaluations; and to identify problems with waste form development and evaluation.

II. Material Properties

This section contains individual presentations on the fundamental understanding of the properties of glass and crystalline ceramics relevant to their use as radioactive waste hosts.

III. Group Reports on the Behavior of Glass and Crystalline Ceramics as Waste Forms

This section contains consensus reports by groups of individuals attending the workshop evaluating the present state of our knowledge on the fundamental behavior of glass and crystalline ceramics as radioactive waste forms.

The Appendix contains the agenda of the workshop and the list of participants and attendees.

It is the intent of this report to assist in focusing attention on an important area of materials application to energy technology development. The meeting and the report are to be considered as only part of the existing and continuing investigation of materials for radioactive waste hosts.

WASTE FORMS

OVERVIEW OF HIGH LEVEL WASTE MANAGEMENT

R. W. Ramsey and C. R. Cooley

Division of Waste Management, Production, and Reprocessing
U. S. Energy Research and Development Administration

INTRODUCTION

On behalf of ERDA, I want to thank you for your interest in attending this workshop on a very timely and technically interesting subject, glass and ceramics as a solid form for high-level waste. Your interest in this workshop is the kind of attention that can assure that the technologies being developed for high-level wastes are appropriate for the near term as well as longer term applications. The wide range of technical disciplines which you represent is certainly outstanding in the field of glass and ceramic materials.

In this presentation we will review some of the basic concepts to provide an overview and a frame of reference for the workshop. These include:

- Source of High-Level Liquid Waste
- Amount of High-Level Liquid or Solid Waste
- U.S. Plans and Objectives
- U.S. Solidification Methods
- Overall Schedules
- Developments in Other Countries

The developments, plans, schedules, priorities, and industrial choices for solidifying waste are influenced by several important considerations listed in Table

Table 1

Considerations for High-Level Waste Solidifications Technology

Public Perception
Technical
Environmental
Produceability
Cost
Availability
Time Perspective

The workshop will concentrate on the technical considerations which provide the basis for a number of the other considerations. While discussing the technical considerations keep in mind these other considerations. Accordingly, we must translate our technology into intelligible terms to achieve greater public understanding. We must provide the basis on which environmental judgments can be made. We must assure regardless of the waste form selected, that it is reliably produceable in equipment that can be operated reliably and safely under radioactive conditions at a reasonable cost. We must assure that our choices and our developments are attainable in a time scale that permits the application of the technology to actual requirements. This implies that some attractive waste form may be identified but may not be used initially (or ever) because it requires more time to establish the process in competition with the safety, simplicity, or reduced costs of existing waste form processes. Waste form improvements undoubtedly will come with time, but the selection of different material forms must be placed in perspective relative to their availability and timeliness. It takes much less time and money to develop a waste form in the laboratory than to develop a process for a plant. Therefore, some good candidates will not get chosen for large scale process development.

There are two distinct time periods in the management of waste when its form is a primary interest. The first is that finite period of time before waste is placed in terminal storage at the Federal repository during which the waste form properties must

be clearly defined and predictable. The second involves the long-term isolation of the radioactive material to be established by the geologic site. Since we are relying on the geology of a site as a primary barrier during this latter time, changes in the properties of the solid by orders of magnitude may be acceptable. However, each time period requires technical information to analyze the contribution and importance of waste form to reducing risk. Keep this perspective in mind in your discussions and you can help us to develop priorities among the many promising avenues of approach to the development of radioactive waste forms.

SOURCE OF HIGH-LEVEL LIQUID WASTE (HLLW)

High-level waste originates from reprocessing of spent nuclear fuel (Figure 1). In reprocessing, the nuclear fuel is cut and sheared to produce segments about 1 to 3 inches long. These pieces are placed in a dissolver where the addition of nitric acid dissolves the fuel and produces a solution containing uranium, plutonium and fission products along with insoluble residues. The solution is chemically adjusted and subjected to solvent extraction which transfers the uranium and plutonium into an organic solvent. The fission products are not readily extractable and remain in the nitric acid solution from the first cycle of solvent extraction. This solution, concentrated to reduce the volume to about 600 liters per metric ton of fuel processed, is a slurry-like liquid defined as high-level liquid waste.

QUANTITY OF HIGH-LEVEL WASTE

The quantity of high-level waste in a solidified form is in direct proportion to the amount of fuel which is processed after being discharged from a reactor. The concentration and composition of waste fission products is a function of the fuel exposure, flux (function of specific power) the neutron spectrum, and the age of the

fuel since exposure in the reactor. About one gram of fission product nuclei is produced per megawatt day of fission energy produced (thermal energy).

A typical quantity of spent fuel discharged from a 100 MWe reactor is about 30 metric tons per year based on 30,000 megawatt days (thermal) and 80% operating time during a single year of operation. Reprocessing 30 metric tons of fuel produces a high-level liquid waste which when solidified has a volume of about 0.1M^3 per metric ton. Thus, the volume of solidified waste would be no more than 3M^3 for the annual 30 metric tons of fuel from the reactor. This would fill about 15-20 typical metal containers. Total volumes of waste can be projected from the amount of nuclear power expected as shown in Table 2.

Table 2

Projected Amounts of High-Level Waste
(In Year Shown)

<u>Year</u>	<u>GWe from Nuclear</u>	<u>MT Spent Fuel/Yr</u>	<u>Number of containers of waste shipped after 10 years storage*</u>
1985	180	1435	
1990	315	6250	570
2000	640	14040	1990
2010			4470

*Each container will hold approximately 0.2M^3 of solid produced from high-level wastes generated by reprocessing 2-3 metric tons of spent fuel, and having a composition of 20 to 30% fission product oxides in the solid, typical of a glass waste form.

The actual volume of high-level waste is small and the fact that the accumulation of containers could be placed in a space the size of a football field is often quoted. Perhaps a more meaningful perspective on the amount of waste can be obtained by the observation of the glass button shown in Figure 2. If it is assumed that all of the

REPROCESSING - SOURCE OF HLLW

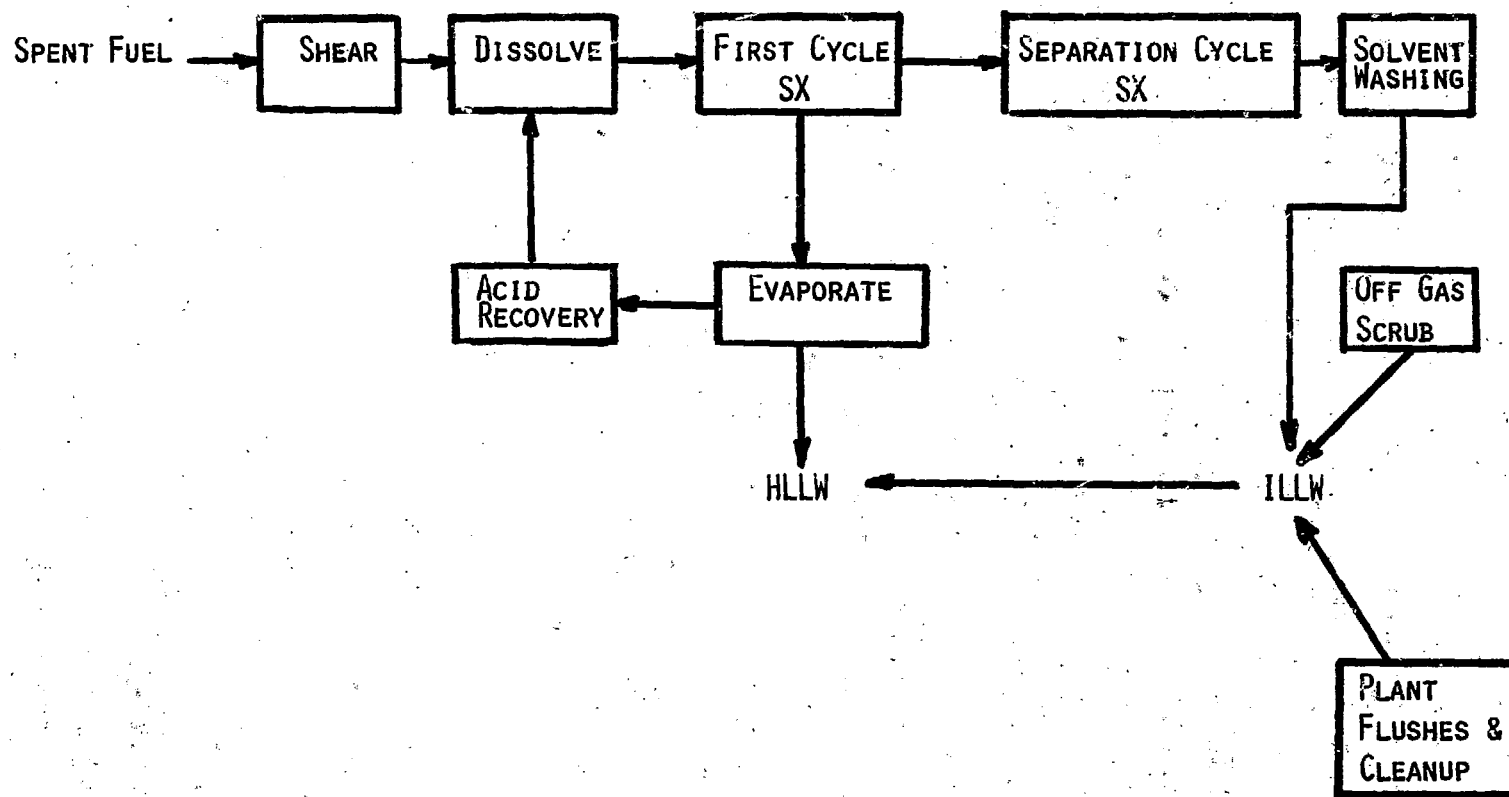


Figure 1. Schematic reprocessing cycle showing the sources of HLLW.

electricity required by an average individual in the United States in a year (9300 Kilowatt-hours) is produced by nuclear power, the amount of high level waste corresponds to the button.

U.S. PLANS AND OBJECTIVES

Our foremost objective in waste management is to provide technology which enables commercial design, licensing and operation of plants for solidifying and immobilizing radioactive waste materials and to provide facilities in various deep geologic formation at multiple locations in the USA which will safely dispose of the Commercial radioactive waste which must be delivered to a Federal Repository for terminal storage.

Why solidify or immobilize waste? Answers to this question provide the general basis of our programs as summarized in Table 3.

Table 3

BASIS FOR DEVELOPMENT PROGRAMS ON SOLIDIFICATION-IMMOBILIZATION OF WASTE

- Solidification provides an improved margin of safety during handling, storage and shipment.
- Isolation of solids in geologic formations is the best near-term disposal method.
- Federal custody of solidified high-level waste is now required by Federal regulations (10 CFR 50 Appendix F).

Improved safety during handling and shipping can be achieved by immobilizing or fixing the waste as a solid. Such physical properties as leachability of fission products by water, dispersion of radioactivity in air and resistance to impact have been considered in the development of the solid forms to improve the associated safety. For high level waste most of the research and development has been directed to conversion of liquid HLW to calcines and glasses or similar vitreous forms, not only in the United States but in other countries using nuclear power.



How We Can Handle Nuclear Waste

A promising form to store the high level waste resulting from nuclear power is in relatively insoluble borosilicate glass. This waste glass for one person, if all U.S. electricity were produced by nuclear power, an individual's lifetime share would be about a cupful. Processes to incorporate waste in glass are developed. The product is a highly stable material well-suited for geologic isolation.

Figure 2. Volume of High-Level Waste in Glass Form Equivalent to all Nuclear Electricity for One Person per Year.

Title 10 of the Code of Federal Regulations, Appendix F, Contains the current requirements for high level waste and are summarized in Table 4.

Table 4

OF FEDERAL REGULATIONS REQUIREMENTS
FOR HIGH LEVEL WASTE

- 5. Liquid waste shall be converted to a dry solid within generation.
- High-level waste shall be delivered to a Federal repository within 10 years after generation. (Separation from fuel in reprocessing)
- Dry solid shall be chemically, thermally and radiolytically stable enough to prevent pressurization of a sealed container within 90 days after receipt at the Federal repository.

What do we hope to achieve by solidifying waste? With the above as a basis for solidification the general objectives of solidification are as listed in Table 5.

Table 5

SOLIDIFICATION OBJECTIVE

Provide a Highly Immobile Solid Form of Waste Which Fixes Fission Products and Has The Following Properties:

- Not readily airborne
- Not readily leachable
- Chemically, thermally and radiolytically stable
- Placeable in containers for 5-10 years for storage and/or shipping prior to geologic isolation
- Heat dissipation sufficient to keep the temperature below processing conditions and low enough to be thermally stable
- Produceable at a reasonable cost

BARRIERS TO THE ENVIRONMENT

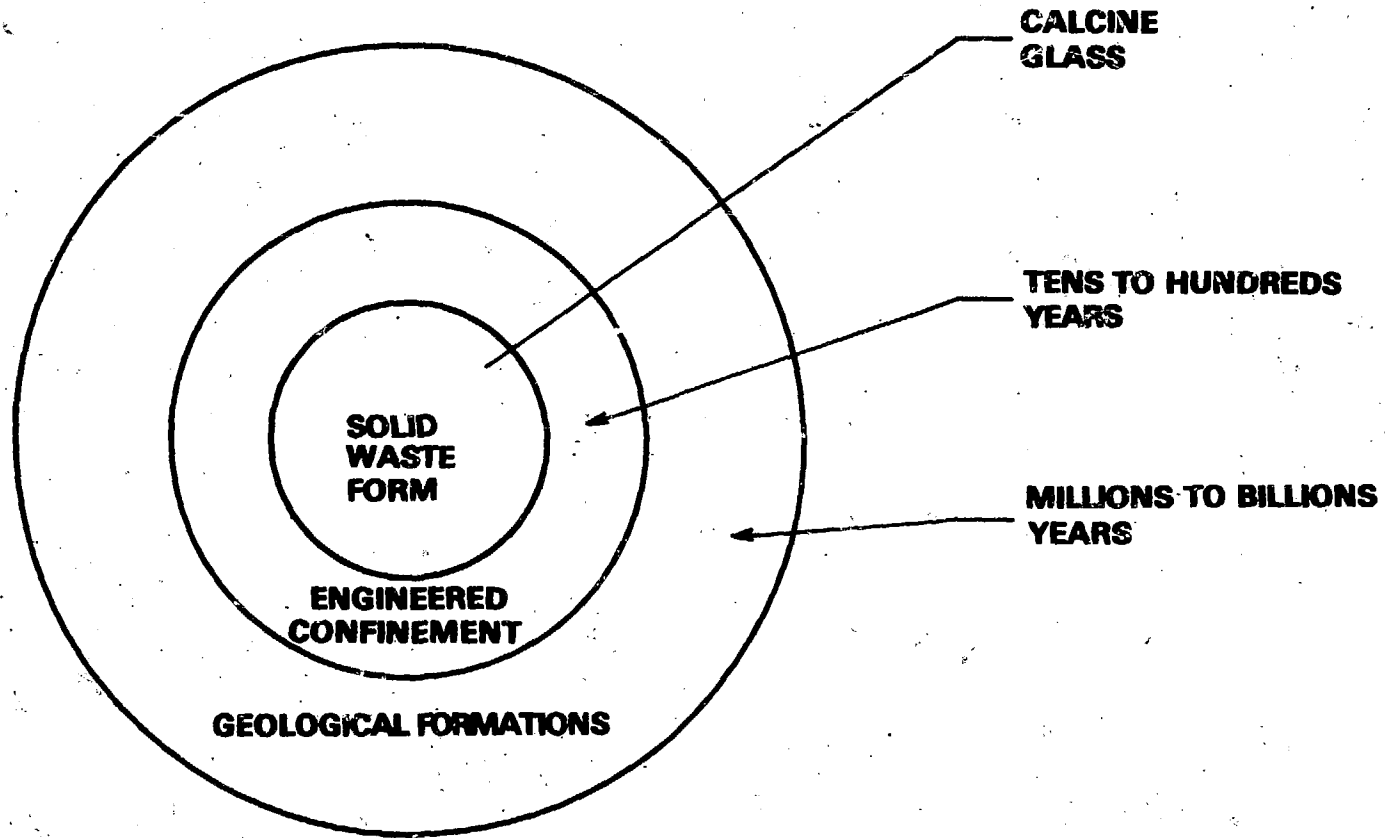


Figure 3. Barriers to the Environment

The major importance of solidification involves improved safety during the near-term handling, storage, shipment and the disposal operations at the Federal repository. However, there are other benefits. The treatment of waste to achieve solid stable forms may provide one more layer of protection and insurance for long-term isolation of waste. Figure 3 indicates the general boundaries of protection. The fact that solids have desirable properties for isolation of waste may provide an added margin of long-term safety. Although we think that engineered features involving canisters or other containment may provide a temporary barrier; we believe that we can rely on the stability of certain geologic formations as a mainline isolation barrier for hundreds to thousands of years once any solid is placed in geologic isolation.

Glass or vitreous waste forms are being favored by commercial reprocessors. Glass provides an immobile form of waste. It can be easily made in simple equipment, and has improved heat conduction over calcine. Dissipation of the heat load from radioactive decay of fission products is necessary during early years to keep temperatures in the waste material in a stable region under normal conditions. Typically, the heat generation in high-level waste decreases with time as shown in Table 6.

Table 6

HEAT GENERATION FROM RADIOACTIVE DECAY
IN HIGH-LEVEL WASTES

<u>Time out of Reactor</u>	<u>KM/MTU*</u>	<u>KW In One Can of Waste**</u>
160 day	18.5	45
1 year	9.2	25
10 years	0.86	2

* Based on 25,000 MWd/MTU and 35 MW/MTU.

** Based on 0.2M³ per container and 2.5 MT/container.
Most waste will be well decayed from fuel storage
in early reprocessing operations.

COMPOSITION AND PROPERTIES OF HIGH-LEVEL WASTE

A typical composition of high-level liquid waste (HLLW) is shown in Table 7. A major constituent is nonradioactive material such as iron and chromium from corrosion of the processing equipment and also chemicals which have been added to the process to obtain chemical or nuclear conditions required for reprocessing (e.g. Gd or Cd as poisons for criticality control). These inerts and the fission products in an aqueous nitrate solution or slurry form constitute liquid high-level waste. Actually only about 1 gm of fission products is produced per thermal Mwd so a ton of fuel contains about 30 kilograms of fission products. The composition of high-level waste may be altered by choosing to include other waste streams such as those from subsequent decontamination steps as a part of high-level waste, particularly those streams with enough radioactivity to require shielding. This provides a convenient dilution of the HLW and a potential cost saving in storing and disposing of other waste without significantly increasing the number of containers of high-level waste. It eliminates the need for a separate processing system for such wastes. It does, however, increase the size of the container as more non-heat-generating chemical waste is included with high-level waste. A typical example of such intermediate level liquid waste (ILLW) which can be at least partially included, i.e., within limits of compatibility with the solidification process, is shown in Table 8.

The introduction of ILLW with HLLW significantly raises the sodium content of high-level waste and requires compensating chemical adjustments in processes to produce calcine or glass. Alteration of the chemical content is usually done by the addition of iron to compensate for the increased amount of sodium. The principal effect of sodium without compensating iron is to lower the melting point of the waste during certain calcination processes enough that it becomes sticky at the processing temperature. (Sticky calcine can coat processing vessel walls and plug pipes.) The

TABLE 7
COMPOSITION OF HLLW*

Concentration, moles/l @ 378l/MTU			Kilograms Nonvolatile Oxide/MTU		
Constituent	Possible Range	Reference for this Document(a)	Constituent	Reference for this Document	
<u>Inerts</u> (Reprocessing Chemicals)	H ⁺	1-7	2.0	---	
	Na	0-3.0	0.01	Na ₂ O	0.12
	Fe	0.05-1.4	0.054	Fe ₂ O ₃	1.6
	Cr	0.01-0.04	0.0096	Cr ₂ O ₃	0.28
	Ni	0.005-0.02	0.0034	NiO	0.19
	PO ₄ ³⁻	0.025-0.30	0.042	P ₂ O ₅	1.1
	SO ₄ ²⁻	0-0.90	0	SO ₃	0
	NO ₃ ⁻	2.7-20	3.6	---	---
	F ⁻	0-0.25	0	F ⁻	0
	Gd(b)	0-0.2	0.150	Gd ₂ O ₃	10.0
	B(b)	0-5.0	0	B ₂ O ₃	0
	Cd(b)	0-1.5	0	CdO	0
			Subtotal	13.0	
<u>Fission Products</u>	Rb	(c)	0.0095	Rb ₂ O	0.34
	Sr	(c)	0.017	SrO	0.68
	Y	(c)	0.0095	Y ₂ O ₃	0.41
	Zr	(c)	0.074	ZrO ₂	3.5
	Mo	(c)	0.071	MoO ₃	3.9
	Tc	(c)	0.017	Tc ₂ O ₇	1.0
	Ru	(c)	0.044	RuO ₂	2.2
	Rh	(c)	0.011	Rh ₂ O ₃	0.53
	Pd	(c)	0.030	PdO	1.4
	Ag	(c)	0.0015	Ag ₂ O	0.067
	Cd	(c)	0.0016	CdO	0.078
	Sn	(c)	0.0009	SnO ₂	0.052
	Sb	(c)	0.0002	Sb ₂ O ₃	0.013
	Te	(c)	0.0078	TeO ₂	0.47
	Cs	(c)	0.039	Cs ₂ O	2.2
	Ba	(c)	0.023	BaO	1.3
	La	(c)	0.018	La ₂ O ₃	1.1
	Ce	(c)	0.034	CeO ₂	2.2
	Pr	(c)	0.016	Pr ₆ O ₁₁	1.1
	Nd	(c)	0.055	Nd ₂ O ₃	3.5
	Pm	(c)	0.0005	Pm ₂ O ₃	0.035
	Sm	(c)	0.012	Sm ₂ O ₃	0.80
	Eu	(c)	0.002	Eu ₂ O ₃	0.13
	Gd	(c)	0.001	Gd ₂ O ₃	0.076
				Subtotal	27.0
<u>Actinides</u>	U	0.011-0.22	0.053	U ₃ O ₈	5.7
	Np	(c)	0.003	NpO ₂	0.31
	Pu	0.0001-0.006	0.002	PuO ₂	0.17
	Am	(c)	0.009	Am ₂ O ₃	0.96
	Cm	(c)	0.003	Cm ₂ O ₃	0.26
				Subtotal	7.4
			Total	47.0	

- a. The reference HLLW is representative of a large state-of-the-art commercial reprocessing plant such as BNFP.
- b. Potential soluble poisons which may be used during fuel dissolution.
- c. Depends upon burnup of the fuel being reprocessed, should not vary over a factor of two from the reference waste composition (burnup=25,000 MWD/MTU).

* Reference: ERDA Report No. 76-43

Table 8
PROPERTIES OF INTERMEDIATE LEVEL WASTE*

	<u>g/liter^(a)</u>	<u>Ci/year</u>	<u>Kg/year^(a)</u>
<u>Chemical Composition</u>			
NO ₃ ⁻	400	--	66,000
Na	150	--	24,750
Hg	15	--	2,475
Ca, Mn, SO ₄ ⁻⁻ , Cl	1 each	--	165 each
K, Fe, Ag, F	0.5 each	--	82 each
Misc. Chem. ^(b)	minor	--	-----
<u>Radioactivity</u>			
U	20	--	3,300
Pu	0.05	--	8.25
I ^(c)	1.8	2300	297
Fission Products ^(d)	trace	3300	-----
<u>Physical Properties</u>			
Volume, liter/year ^(e,f)		165,000	
Solids ^(a)			97,000
Density (estimate)	1400		
Heat Generation (W/l)		0.01-0.1	

a. Based on ~42% dissolved solids.

b. Oxalate, citrate, phosphate, acetate, ammonium, chromate, surfactants, detergents, etc.

c. Based on ~100% of iodine in this stream, 79% ¹²⁹I, 21% ¹²⁷I by weight, and 98% ¹³¹I, 2% ¹²⁹I by activity, at 320 days following discharge from reactor core.

d. Based on 2.2 Ci/MTHM. These values may be low by a factor of 10 or more, compared to values based on other estimates. Activity contributed primarily by fission product Ru, Rh, Zr, and Nb.

e. Based on 110 liters per MTHM, 1500 MTHM per year.

f. It is estimated that spent, combustible solvents will be generated at a FRP at the rate of 0.01 m³/MTU or 15 m³/1500 MTU-year, (8) the reference process includes combustion of the solvent.

* Reference: ERDA Report No. 76-43.

inclusion of certain ILLW with HLLW has been tested and equipment performance has been made satisfactory after the compensating adjustments in chemical content are made. The normal composition range for vitreous forms of waste are shown in Table 9. About 20 to 35% of the fission product oxides can be incorporated in a vitreous form.

Table 9

HIGH-LEVEL WASTE BOROSILICATE GLASS COMPOSITION

SiO ₂	25-40%
B ₂ O ₃	10-15%
Alkali Metal Oxides	20-35%
ZnO	0-20%
Waste Oxides	20-35%

USA SOLIDIFICATION METHODS

The processing methods currently receiving the most emphasis in development work are the processes currently preferred by reprocessors. They are discussed below.

1. Fluid-Bed Calciner

Calcination involves heating HLLW to a sufficiently high temperature to remove all of the liquid, to denitrate and to convert the materials into radiolytically and thermally stable oxides and salts. Calcination can, hence, provide a stable material for storage, or a calcine material which can be consolidated into a glass or other immobile forms. Calcination can be accomplished by a number of ways involving simply heating in suitable crucibles (batch pot calcination) or more sophisticated equipment. A fluid-bed or spray calciner or rotary calciner or kiln can be used to obtain continuous processes. One of the most developed methods of producing a calcine in the United States is the fluidized-bed calciner.

One design of a fluidized-bed calciner is shown in Figure 4 for a 1500 MT/yr reprocessing plant. Liquid high-level waste is fed to about a 2-foot diameter process column through a spray nozzle which distributes the waste in a bed of granules which are suspended (i.e. fluidized) in a stream of air. Heat is provided to the bed by introducing kerosene and combusting it directly in the bed. The heat evaporates and denitrates waste and continually deposits the resulting solids as a coating on the granules of the bed which overflow into a container for storage or into feed equipment for further processing. Fine particles are separated from the air and off-gas stream by sintered metal filters. Periodically, a puff of air is injected inside the filters to dislodge the accumulated fines and clean the filters.

A fluidized-bed calciner of slightly different design has been operated in ERDA facilities at Idaho National Engineering Laboratory (INEL) to process high-level waste to calcine since 1963. The fluidized-bed calciner has been tested for use with commercial reprocessing plant waste in engineering developments at INEL and at Pacific Northwest Laboratory, Richland, Washington.

2. Spray Calcination In-Can Melting

The spray calciner in-can melter shown in Figure 5 is also currently one of the favored systems for treating high-level liquid waste to accomplish conversion of the liquid to a glassy form for storage in a Federal repository. The process consists of atomizing the liquid waste by a spray nozzle located at the top of a heated cylindrical column approximately 30 inches in diameter. The atomized waste is dried, calcined to produce a free flowing powder which accumulates in a container situated below the calciner. Sufficient glass forming frit is added to the powder to provide the formation of a molten

mass of glass containing the fission product oxides. After filling, the container is cooled to solidify the glass and serves as the final storage container.

The spray calciner in-can melter process has been tested in a series of operations including various sized units and in radioactive units where containers 8 inches in diameter have been filled. The waste held for observation continues to show that the material is acceptable for Federal storage pending actual standards for disposal. Currently, a non-radioactive full-scale test of the unit is planned in 1977 to verify the design being selected for commercial use. Hot pilot plant tests are planned in 1978.

3. Continuous Melters

Figure 6 shows the present concept for a more advanced continuous melter to replace the in-can unit. The technology is based on high temperature joule-heated electric melters used by the glass industry. In the melters for high-level waste, the calcine is fed along with glass forming chemicals or glass frit as a cold cap above a pool of glass kept molten by passing electric current through the melt. The unmelted material is used in contact with the molten glass. The accumulated melt, continuously overflows or is poured into a receiving container. The continuous melter can be used with any calciner which will deliver calcine to the unit. Direct liquid feeding to accomplish drying and calcination in the cold cap is also being investigated as a method of providing glass from a single unit.

4. Fluidized-Bed Continuous Ceramic Melter

Coupling the continuous melter with a fluidized-bed calciner provides a

FLUIDIZED BED CALCINER

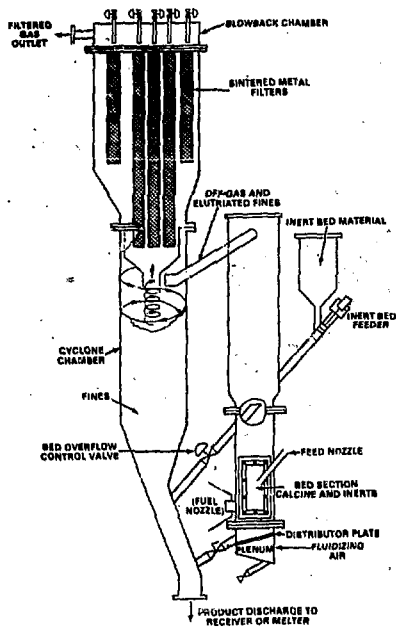


Figure 4. Fluidized bed calciner

SPRAY CALCINER/IN-CAN MELTER PROCESS

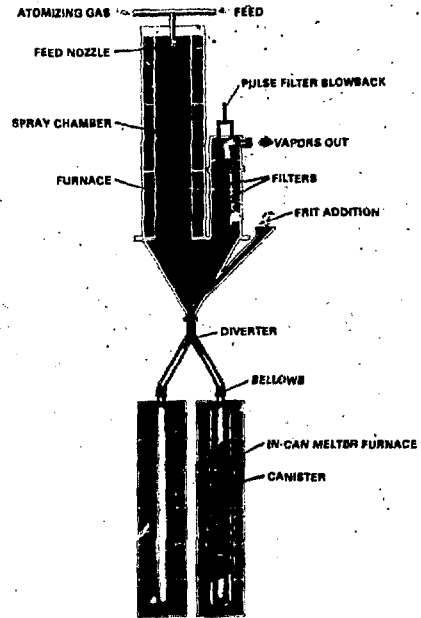


Figure 5. Spray Calciner In-Can Melter

CERAMIC MELTER

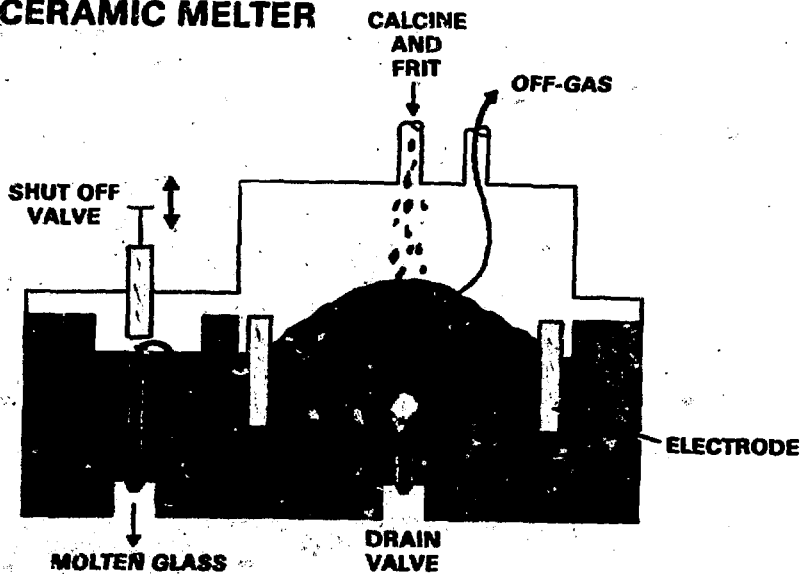


Figure 6. Ceramic Melter

FLUIDIZED-BED - CERAMIC MELTER VITRIFICATION SYSTEM

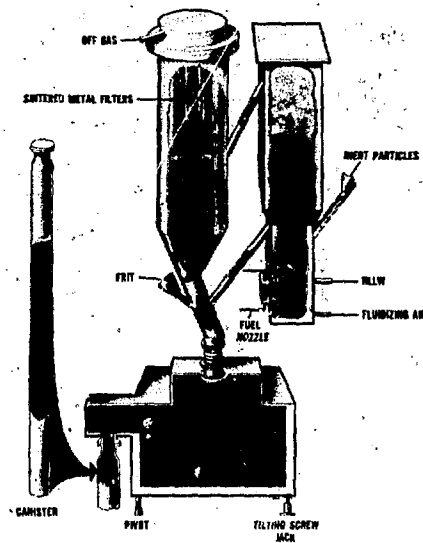


Figure 7. Fluidized bed - ceramic melter vitrification system

SCENARIO OF WASTE MANAGEMENT

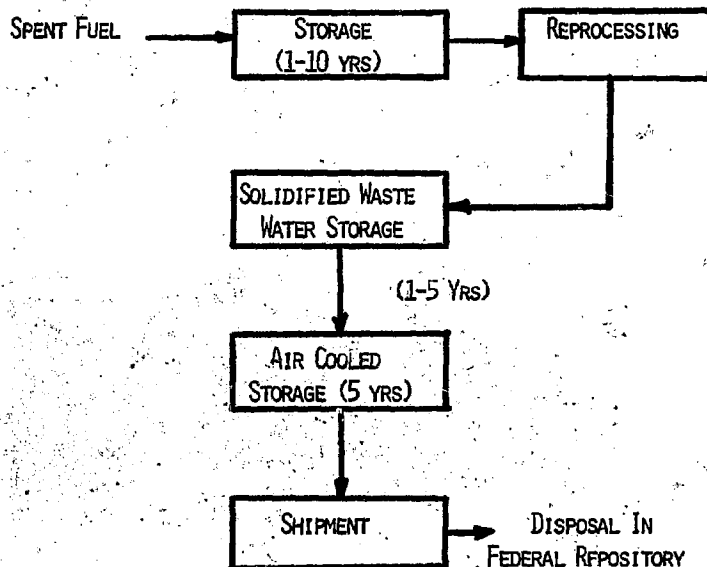


Figure 8. Scenario of Waste Management

solidification system for high-level waste as shown in Figure 7. The fluidized-bed calciner continuous ceramic melter is to be tested using specific reprocessor conditions and designs in the next 4 years including full-scale design verification and remote mock up tests on a non-radioactive basis. Hot pilot plant tests with radioactive waste feed at about 1/5 of full-scale processing rate are also being planned.

WASTE MANAGEMENT SCENARIO

In order to put the total high-level waste management system in perspective let's briefly review a likely scenario, Figure 8.

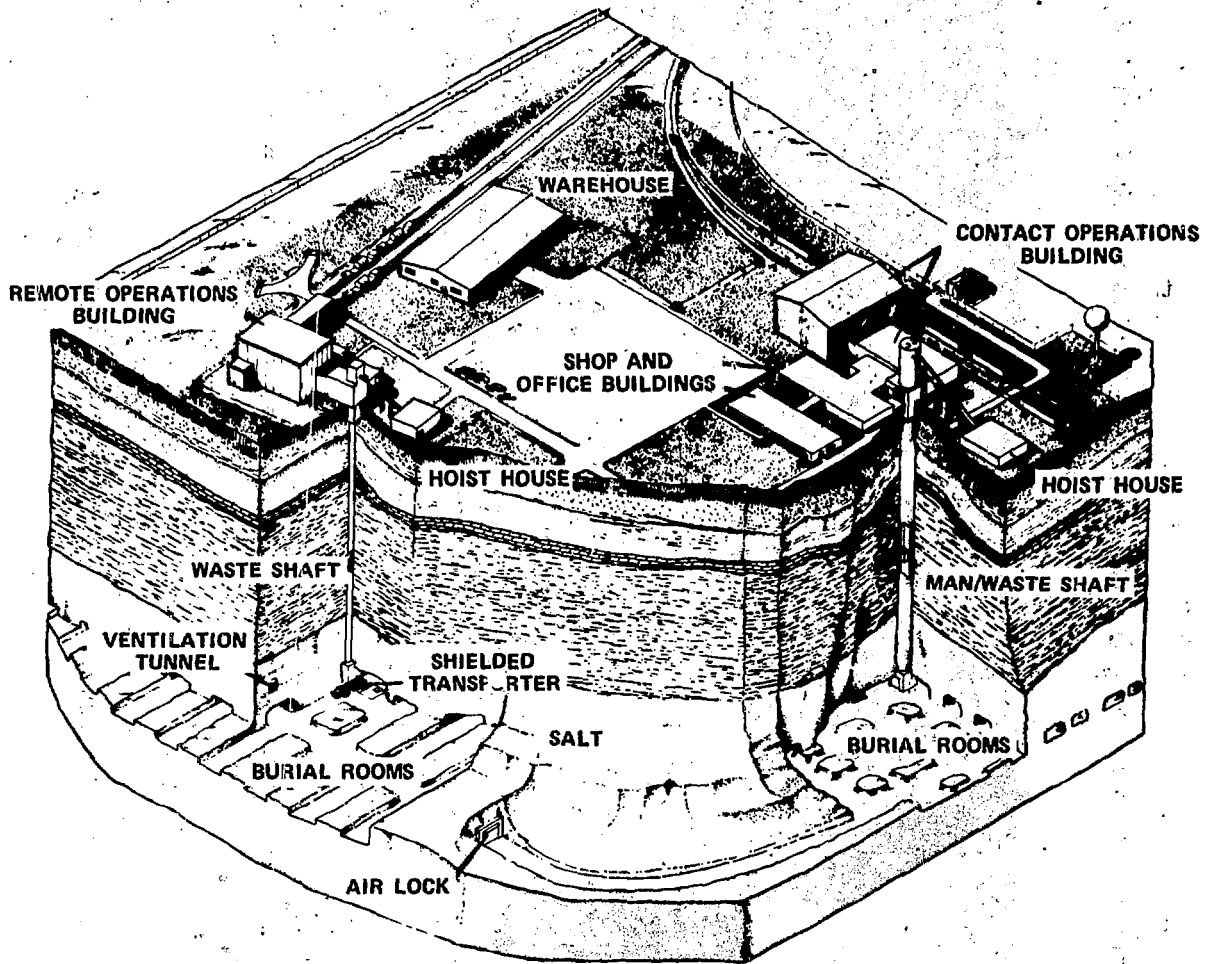
Spent fuel from a nuclear reactor is shipped to a 1500 MT/day reprocessing plant where the fuel is processed perhaps a year after discharge from the reactor to produce a liquid slurry of high-level waste which is routed to a process tank with sufficient hold up to accumulate perhaps an additional year of storage as process surge capacity. The liquid waste is sent to an evaporator-denitrator to concentrate the waste further and remove nitric acid for reuse in the plant. The waste is blended with other waste such as intermediate level liquids, chemically adjusted and pumped to a 30-inch diameter spray calciner with a 12-20 inch diameter in-can melter in two positions heated to 900-1000°C. Up to two canisters are filled per day and, following filling, are cooled and conditioned by temperature control during cooling to provide good material properties of the glass and stress control in the canister. The canisters are then removed from the furnace, sealed by welding the fill cap, leak checked, surface cleaned, and placed in storage in a purified and cooled water storage pool. After storage in the pool for up to 5 years, the containers are removed, inserted dry into a licensed shipping cask similar to a spent fuel cask and shipped by rail or truck to the Federal repository.

At the repository containers are unloaded from the cask and transferred into the underground Federal repository and into a transport cask which places the container in a predrilled and properly spaced hole in the floor of the underground cavern or vault as shown in Figures 9 and 10. The hole is back filled after placement of the container. Eventually all holes in the cavern floor are filled and the cavern is sealed reestablishing as closely as possible, the natural conditions or improved conditions (better than the original geologic formation). The solidified waste remains as an investment in the host geologic formation.

Where are the sites for Federal repositories located? No definite selection has been made, but a carefully coordinated investigation of sites has been started this year on some of the most attractive locations based on known geology. The general areas of possibilities are shown in Figures 11, 12, and 13. The entire program cannot be covered here, but the sequential technical aspects of development of a site include:

1. Identification of geologic formation of interest
2. Reconnaissance to provide geologic data
3. Specific geologic studies of an area to determine an actual site
4. Generic in-situ tests at sites
5. Detailed confirmation studies to establish suitability
6. Construction of repository
7. Repository operation with retrievable capability
8. Conversion to permanent disposal repository

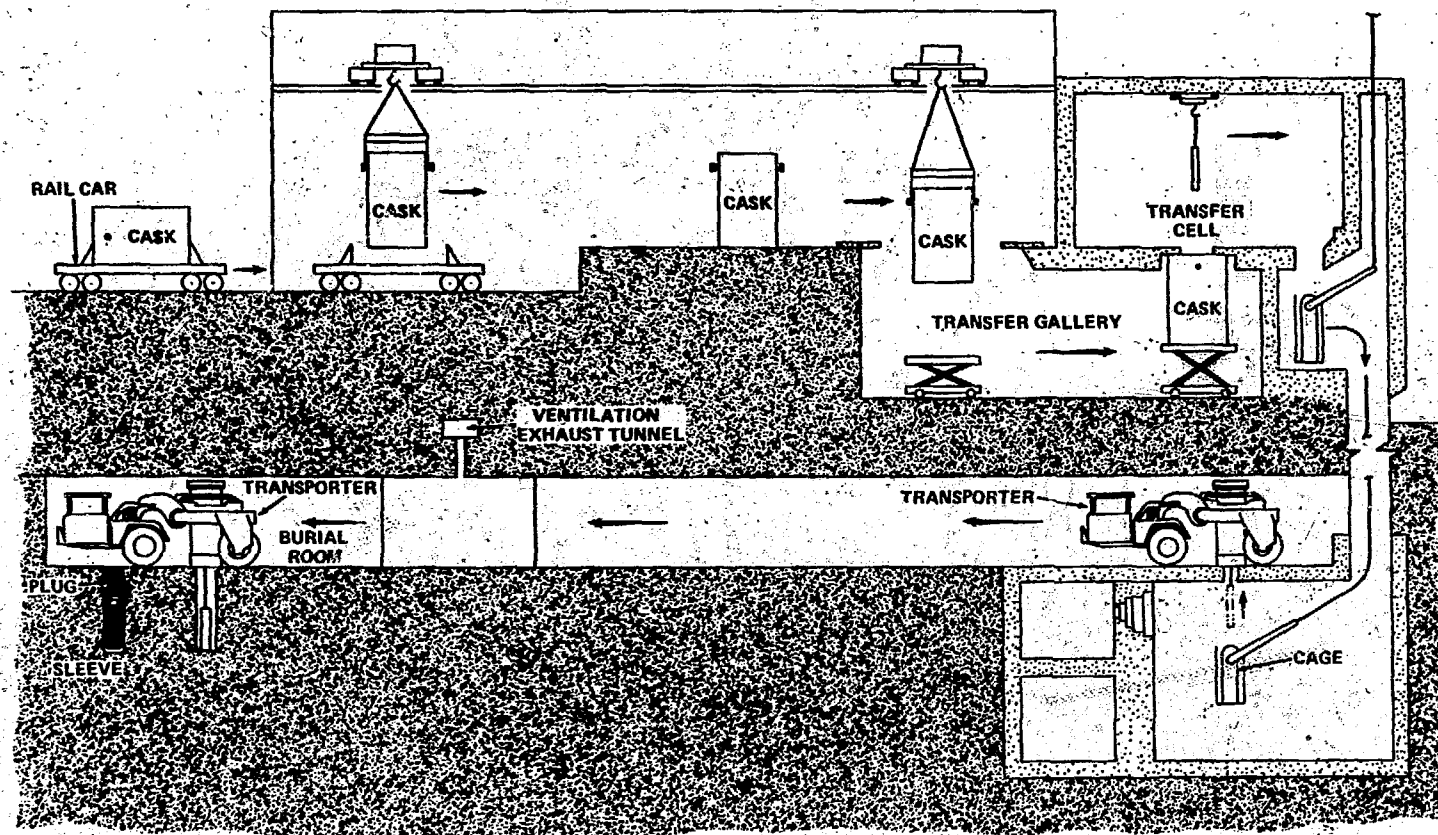
The present plan is to identify and construct six repositories. The first two are planned for salt formations about 1985. The remaining four will probably be divided between argillaceous and crystalline rock formations and should be available by 1990.



PILOT PLANT CUTAWAY

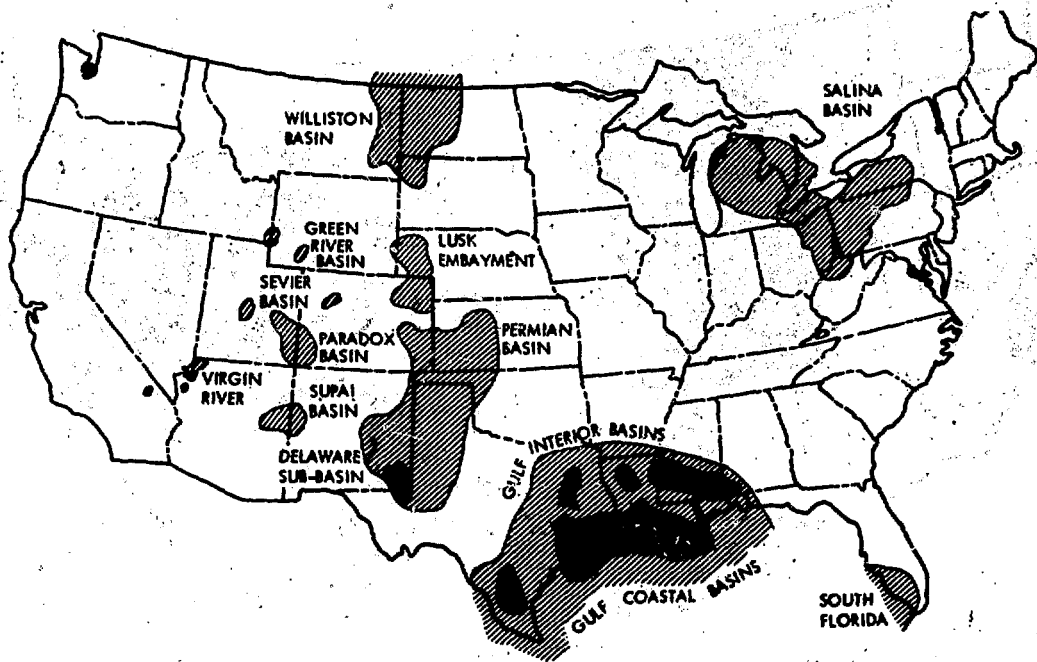
Figure 9. Cutaway Drawing of the Proposed Federal Underground Waste Repository

REMOTE OPERATIONS SCHEMATIC



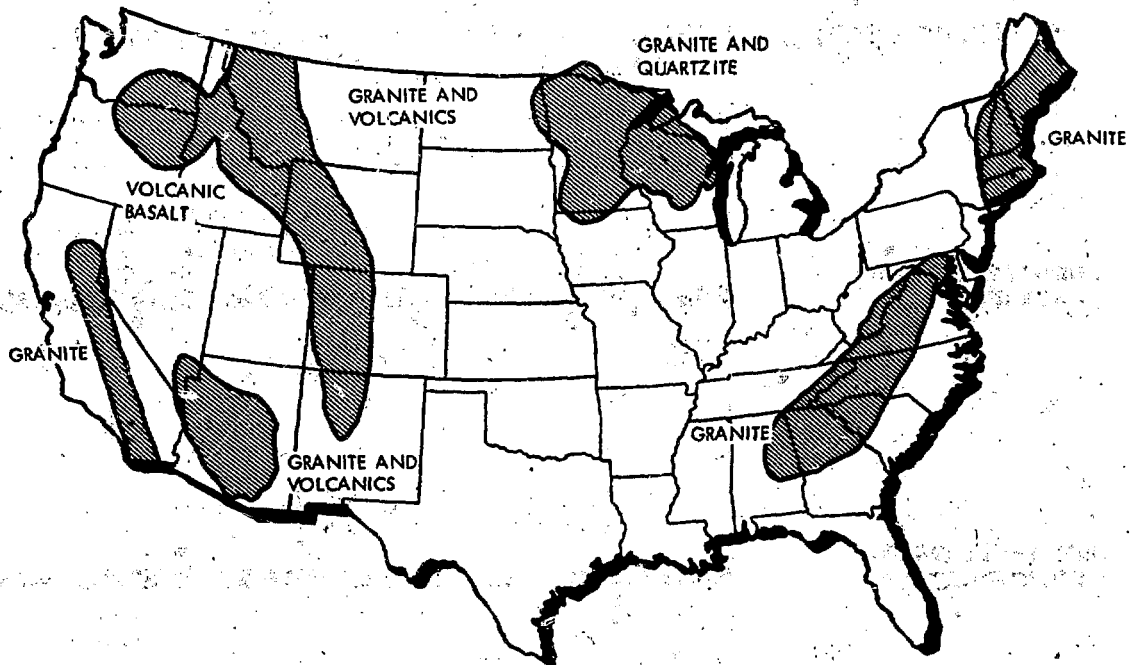
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Figure 10. Schematic of the Remote Underground Storage Operations in the Federal Repository.



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Figure 11. Rock Salt Deposits in the United States



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Figure 12. Crystalline Formations in the United States

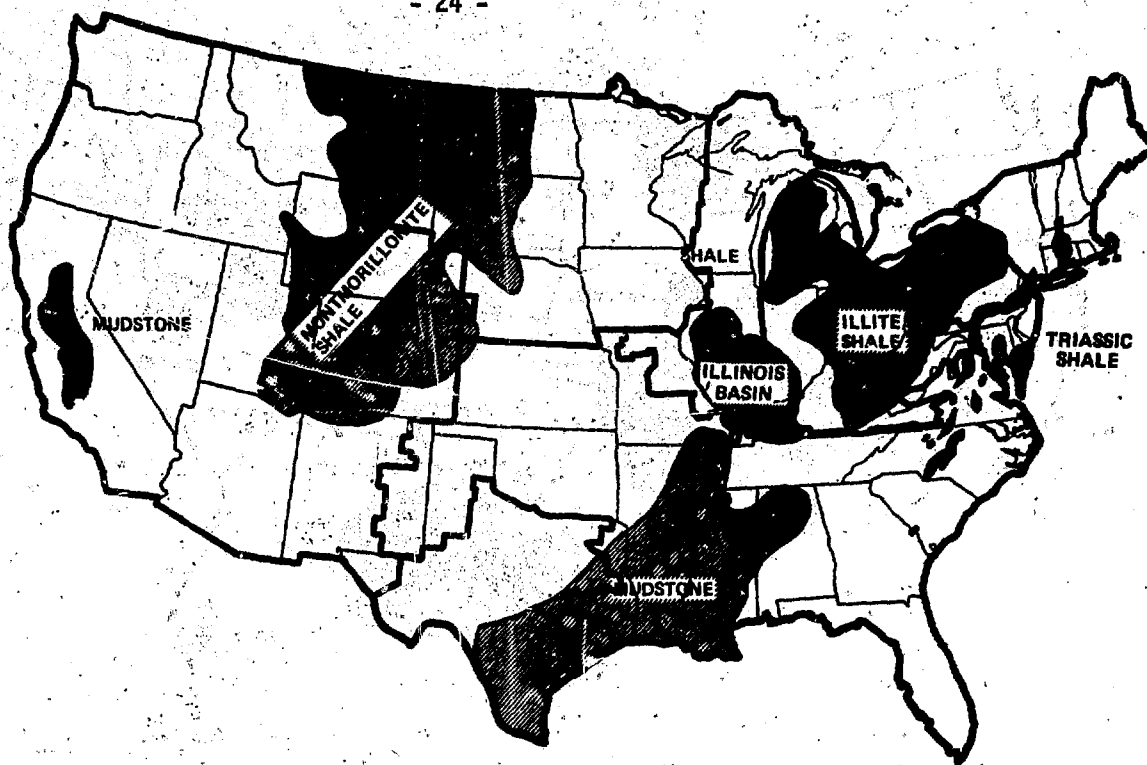


Figure 13. Distribution of Shale Rocks in the United States

TIMETABLE FOR COMMERCIAL RADIOACTIVE WASTE PROGRAM

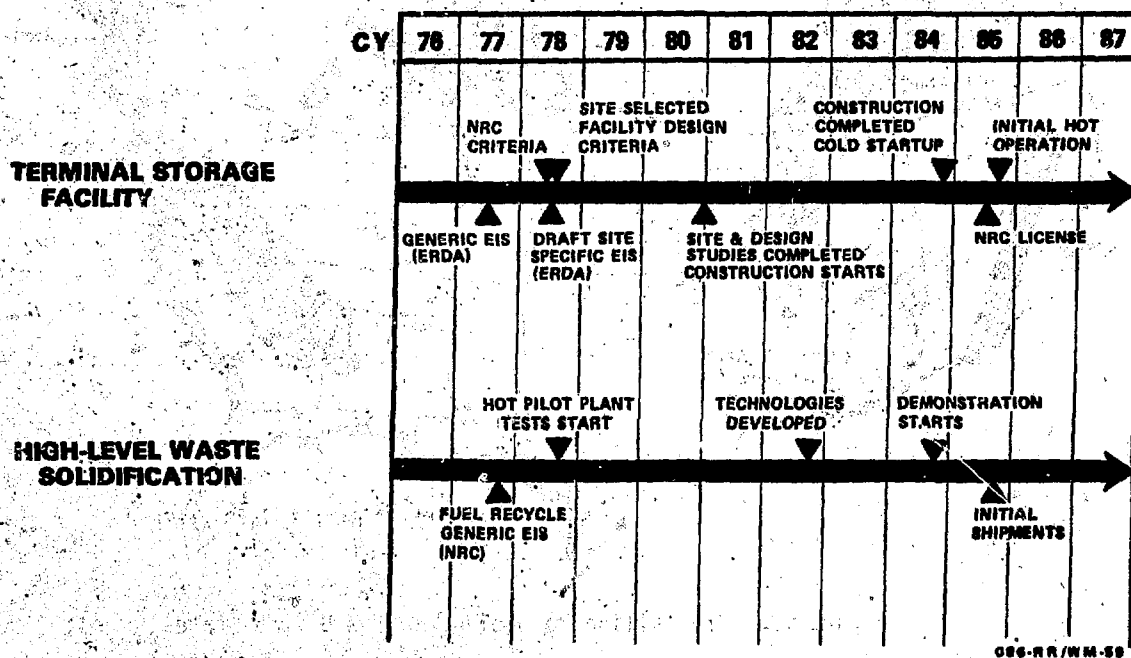


Figure 14. Timetable for Commercial Radioactive Waste Program

OVERALL SCHEDULES

The overall schedules in the U.S. are shown in Figure 14. The development of the technology for solidification is currently scheduled to make the necessary information available within the next 3 years which would permit a commercial organization to design and construct a solidification facility. A commercial demonstration producing canisters of waste could start as soon as 1984. The first terminal storage facility would be available in 1985 for placement of some canisters for testing of the facility.

DEVELOPMENTS IN OTHER COUNTRIES

As each foreign country has evaluated their future requirements for energy, each has planned to place an increasing reliance on nuclear power. Associated with their emphasis on nuclear power has been a development program directed towards the disposal of high-level waste. In Table 9 are listed some of the countries which are more advanced in their developments. In nearly all cases some form of glass is under investigation currently as the most attractive method of providing a solidified form of high-level waste. A number of processes or ways of producing glass have been studied and emphasized primarily because of the necessity of being able to know how one can produce a glass under the constraints imposed by equipment in a radioactive situation. The equipment requirements are complex and opinions vary on how it can best be done. Therefore, each country has a development program to determine if the equipment can function properly and produce reliable forms of glass as waste. Most countries have now developed one or more equipment arrangements to produce a glass. Accordingly, in the next few years, we expect to see more emphasis on identifying the conditions under which the equipment should be operated to produce a desirable form of glass. There are other forms than glass, but they are not as widely developed and it is not known with complete surety that the equipment requirements have been established.

Table 9

HIGH LEVEL WASTE MANAGEMENT PROGRAMS IN OTHER COUNTRIES

<u>Country/Facility</u>	<u>Process</u>	<u>Solid</u>
UK	Harvest - Rising Level	Borosilicate Glass
France	AVM/AVH - Rotary Calciner Continuous Metallic Melter and Ceramic Melters	Borosilicate Glass
FRG	VERA - Spray Calciner Metallic Melter	Borosilicate Glass
	Liquid Fed Ceramic Melter, Joule Heated	Borosilicate Glass
	Drum Drier - Melter	Borosilicate Glass
FRG - Eurochemic	LOTES - Stirred Bed Calciner	Aluminum Phosphate Pellets in Metal
FRG - Eurochemic	PAMELA	Phosphate Glass in Metal
USSR	Fluidized Bed Calciner* with Concrete Crucible	Phosphate Glass
	Liquid Fed Ceramic Melter, Joule Heated	Phosphate Glass
	Preliminary	Basalt-Like

* 10-20 year aging and removal of Sr and Cs

Each country is on a time scale where processes will be demonstrated radioactively in the 1980's. Pilot plants are prevalent from now to 1980. France is within a year of operating a hot pilot plant facility at Marcoule. The U.S. hot pilot plant tests are planned in 1978 to further validate experiments conducted in the late 1960's when a series of hot pilot plant tests were completed on phosphate glass-like materials and borosilicate glasses.

GLASS AS A WASTE FORM: OVERVIEW AND PROCESSING CONSIDERATIONS*

J. E. Mendel

Pacific Northwest Laboratory

INTRODUCTION

Glass has been selected as a suitable form for the immobilization of high-level radioactive waste in this country, and in Russia, India and the western European countries. The selection is based on twenty years of R&D, much of which has been quite process oriented. The purpose of this workshop is to emphasize the materials aspects of the waste form rather than processing. However processing cannot be omitted from waste form considerations completely. The fact that the processing must be done in a highly radioactive environment imposes very real restrictions during processing.

In this paper I will first give an overview of the properties desired in solidified HLW, i.e., what is it we want to make and why? Then I will describe how it is made, and the considerations that must go into the design of the manufacturing process.

WASTE FORM REQUIREMENTS

The basic goal is to design a waste management system which assures the radioactivity in HLW is kept out of the biosphere. Man's surveillance can be assumed to continue for a few generations to correct malfunctions in the system, if any occur, but ultimately isolation of harmful radioactivity must be assured without need of surveillance. The properties of the waste form are an integral part of the waste management system that is being designed for the U.S. The

* Work performed under ERDA Contract EY-76-C-06-1830.

system requires that the waste form have the following properties:

- . Transportable
- . Heat and Radiation Resistant
- . As Nondispersible as Reasonably Achievable

1. Transportation Requirements

High-level liquid waste will be solidified at its point of origin, the reprocessing plants. From there it must be transported to Federal repositories for storage in geologic isolation. Initially, the reprocessing will be done in the southeastern part of the country. Many scattered locations are being considered for the Federal repositories and transportation of the solidified HLW for distances of 1-2000 miles could be required.

Transportation requirements place two general criteria on the waste form. It should have as small a volume as possible to minimize the number of trips required and it must be contained in convenient-sized packages. Waste loadings of 20-40 wt% in glass are sought and it is to be "packaged" in hermetically-sealed steel cylinders each weighing less than a ton.

It should be noted that the present Federal regulation, (1) on the handling of HLW is addressed mainly to the transportation requirements. It specifies that the waste must be solidified for safety in transportation. It places no restrictions on the properties of the solidified waste except that it not react to deleteriously effect the integrity of the canister until at least 90 days after emplacement in the geologic repository.

2. Heat and Radiation Resistance Requirements

The unique features of HLW, aside from its complex chemistry, are very high radiation and associated self-heating. These impose special stability criteria on the solidified waste; the effects of temperature and radiation must be understood well enough so that they can be extrapolated to very long times. Just how long is still being evaluated--certainly it is vital to predict stability for several hundred years

until the ^{90}Sr and ^{137}Cs have decayed, and it is desirable to understand behavior for many thousands of years.

3. Dispersibility

As stated above, solidified waste is only part of a waste management system, all parts of which are designed to prevent dispersion of radioactivity. Thus the nondispersible characteristics of waste glass may be considered as additional backup in a system designed to feature redundant protection. For example, when the glass is made it is immediately placed in a sealed steel canister which affords one layer of protection. The waste glass canisters are then stored in a water basin under 15 feet of water in a protective building to allow much of the short-lived activities such as ^{144}Ce , ^{106}Ru and $^{95}\text{Zr-Nb}$ to decay before shipment to the Federal repository. During shipment the glass canisters are also enclosed in massive, rigorously tested, shielded shipping casks. At the repository they will be buried in carefully selected practically water-free locations 2000 or more feet below the surface of the ground. The depth and selected geology will assure that even if water ultimately contacts the waste glass any leached radioactivity will have a long tortuous path back to the surface. In addition to the long path, sorption and precipitative reactions will occur all along the way which will further greatly slow the effective release.

Because the waste form is only part of a redundant system of protection NEPA guidelines can be applied to the requirements concerning its dispersibility, i.e., it should have as low a dispersibility as reasonably achievable. As the state-of-the-art advances it will be possible to further improve the nondispersibility of the waste form.

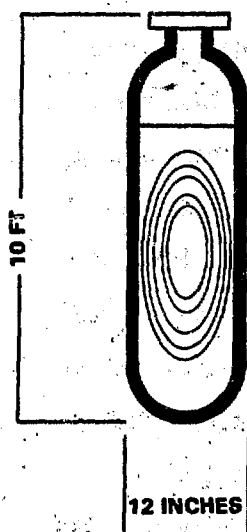
CHARACTERISTICS OF TYPICAL HLW GLASS CANISTER

The characteristics of a typical HLW glass canister, as produced by today's technology, are shown in Figure 1. The values shown may be considered representative. In practice there will be considerable variation in all of the values.

The canisters will probably be fabricated from schedule 40 pipe, filled to

TYPICAL HLW CANISTER

MATERIAL OF CONSTRUCTION: 304L SS



	HEAT GENERATION RATE, kW	CUMULATIVE DOSE/GRAM	DOSE-RATE 1 FT FROM SURFACE
1 YR	22	1.0×10^{17}	1.1×10^6 R/hr
10 YR	3.1	2.5×10^{17}	6.2×10^4
100 YR	0.36	7.1×10^{17}	5.8×10^3
1000 YR	0.02	1.5×10^{18}	1.6
10000 YR	0.006	3.0×10^{18}	1.3
100,000 YR	0.003	6.1×10^{18}	0.6

Figure 1. Typical HLW Canister

Table I

DISPERSION MECHANISMS

	Processing	Accident
Volatility		
Particulate Entrainment		
Dissolution		

approximately 90% capacity and seal welded. Most of the R&D experience has been with 304L stainless steel canisters but other alloys with a higher chrome and nickel content are also being considered.

The heat generation rate drops off rapidly during the first 10 years. Special cooling must be provided for the canisters during initial storage and handling. Even after emplacement in geologic storage there will be sufficient heat so that the canisters must be spaced in carefully designed arrays to prevent overheating of the geologic media. The maximum allowable temperatures for other candidate geologic storage media have not been determined. These limits represent the temperature at the surface of the canister. Of course, there is a temperature gradient within the canister, the central zone being hottest. Wayne Ross and Ray Turcotte will describe these internal temperatures and their potential effects on waste glass in more detail.

The dose rate, due mainly to fission products, is still above 10^4 R/hr after 10 years, so massive shielding is required for shipping. At 1000 years, however, the dose rate per canister is only 1-2 R/hr and a few inches of earth will be adequate shielding for the beta-gamma. There will also be a neutron field, not shown here. The neutron field is present because of the actinides in HLW and it is the actinides, through the alpha recoil particles, that present the most potential for radiation damage to the waste glass. The density of cumulative alpha events as a function of time is shown in Figure 1. Ray Turcotte will discuss how the potential for actinide damage to waste glass is being evaluated.

OVERALL REQUIREMENTS FOR HLW GLASS CHARACTERISTICS

The requirement for waste glass that is most difficult to define, and that receives the most attention, is that it be as nondispersible as possible. The three principal mechanisms by which dispersion can occur are shown in Table 1.

Airborne dispersion can occur either through volatility or particulate entrainment. Both occur during processing and a large and complex off-gas treatment system is required to assure that activity from these sources is collected and either recycled

to the process or treated as a separate waste. During accidents, volatility is not considered a potential dispersion mechanism because all constituents likely to volatilize at hydrocarbon fire temperatures ($<1000^{\circ}\text{C}$) will have been removed or stabilized by the even higher temperatures used during solidification. Particulate entrainment must be considered in accident involving great impact or an explosion. Only particles smaller than 10 millimicrons are considered respirable.

The major dispersion mechanism is probably dissolution. It will be impossible to absolutely insure that water doesn't contact the waste glass during its storage in the geologic repository. Transportation accidents can be envisioned in which the waste glass comes in contact with water. A canister leak during water basin storage can be even more easily envisioned. Thus the leachability of waste glass becomes a continuous concern when analyzing almost all aspects of waste glass composition, manufacture, storage treatment and associated thermal and radiation effects. Of course, the total amount leached is a function not only of the innate leachability of the waste glass, but also of the surface area exposed so that any factor that affects surface area also affects the amount potentially dispersed through the leaching mechanism.

The complex interrelationships that must be considered have been described in "A Program Plan for Comprehensive Characterization of Solidified High-Level Wastes, (2)". Figure 2, taken from the program plan document is a matrix showing the factors involved. The main goal of waste form characterization is to obtain data from which quantitative estimates of dispersion can be made in postulated accidents.

Up to five major factors may be required to define the state of the waste glass at any given time. These are the independent variables listed in the matrix in Figure 2. The dependent variables are the glass properties which must be experimentally determined as a function of the independent variables in order to predict dispersibility.

Processing conditions are a most important independent variable in the matrix. The remainder of this paper will be devoted to a discussion of processing, as

REFERENCE MATRIX FOR WASTE FORM CHARACTERIZATION

PROPERTIES OF WASTE FORM AFFECTING POTENTIAL FOR DISPERSION OF CONTAINED RADIOACTIVITY VIA AIR OR WATER			INFORMATION NECESSARY TO DEFINE SOURCE TERM																				
			COMPOSITION & RADIATION DOSE		TEMPERATURE, TIME AND ENVIRONMENT																		
					FORMULATION	PROCESSING CONDITIONS	STORAGE AND TRANSPORT CONDITIONS	ACCIDENT CONDITIONS	DISPOSAL CONDITIONS														
			RADIOACTIVE INVENTORY IN WASTE NON-RADIOACTIVE CONSTITUENTS OF WASTE	ADDITIVE COMPOSITION						ADDITIVE: WASTE RATIO	PROCESS EQUIPMENT MATERIALS OF CONSTRUCTION	TEMPERATURE	TIME AT TEMPERATURE	RATE OF COOLING	AGITATION (WHERE APPLICABLE)	CANISTER MATERIAL	COOLING MEDIUM	THERMAL HISTORY	TIME	TEMPERATURE TRANSIENTS	IMPACT ENERGY	SURROUNDING MEDIA	TIME IN CONTACT WITH MEDIA
ENVIRONMENTAL REACTIONS	CORROSION OF CONTAINMENT (EXTERNAL)																						
	CORROSION OF CONTAINMENT (INTERNAL)																						
	LEACHABILITY (STATIC SYSTEM)																						
	LEACHABILITY (DYNAMIC SYSTEM)																						
THERMAL STABILITY	VOLATILITY																						
	PHASE CHARACTERIZATION																						
	DEVITRIFICATION (WHERE APPLICABLE)																						
RADIATION ⁽¹⁾ EFFECTS	RADOLYTIC GAS FORMATION																						
	HELIUM SOLUBILITY AND PERMEABILITY																						
	RADIATION DAMAGE																						
BULK PROPERTIES	DENSITY																						
	THERMAL CONDUCTIVITY																						
	VISCOSITY (WHERE APPLICABLE)																						
	THERMAL EXPANSION COEFF.																						
	ELECTRICAL CONDUCTIVITY (WHERE APPLICABLE)																						
PHYSICAL STRENGTH	FRAMIBILITY, MECHANICAL SHOCK																						
	FRAMIBILITY, THERMAL SHOCK																						
	INDUCED STRESSES (DEGREE OF ANNEALING)																						

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

Figure 2. Reference Matrix for Waste Form Characterization

PROCESSING REQUIREMENTS

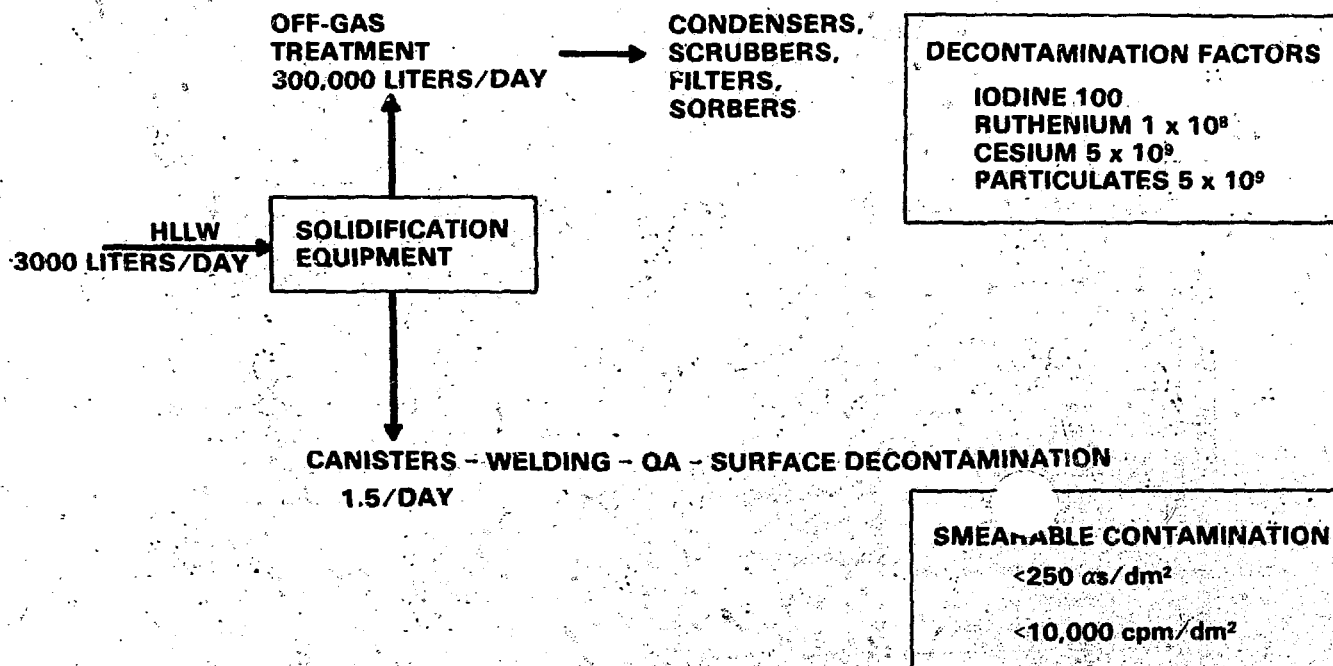


Figure 3. Processing Requirements

illustrated by several well developed waste glass processes, and a discussion of some limitations on processing conditions. Finally I will describe the trends in future processing development.

PROCESSING REQUIREMENTS

The overall processing requirements for a typical HLW solidification process at a 5 MTU/day reprocessing plant are shown in Figure 3. The numbers in Figure 3 are only representative and will vary somewhat in the actual plants. About 3000 liters/day of high-level liquid waste are processed.

1. Off-Gas Treatment

A major proportion of the equipment required for HLW solidification is devoted to cleaning up the off-gas. Different systems may be employed, using various combinations of condensers, scrubbers, sorbers and filters to achieve the decontamination factors shown (decontamination factor = activity in/activity out). The decontamination factor required for iodine is low because only a small amount of radioiodine is present in HLLW.

2. Canister Handling

About 1.5 canisters of glass will be produced per day, the actual number being very dependent on canister size and waste composition. The canisters will be force cooled (annealing by slow cooling to maintain a monolithic casting of glass in the canister is not presently envisioned as part of the U.S. vitrification processes) and seal welded. Then a series of QA measurements will be made. The QA measurements are not yet fully defined but may include vacuum leak checking and/or other types of weld integrity verification, such as dye penetrant testing, ultrasonic wall thickness measurements, and various physical measurements of weight, dimensions and heat content. Finally the canisters will be cleaned as they leave the highly contaminated operating cell to go into the water basin. This decontamination step may use jets of high pressure hot water, with or without added chemicals, or an electropolishing technique.

The net result is that the canister will be subjected to a series of operations, and probably a series of temperature fluctuations, before it ultimately ends up in a water basin under 15 feet of water at 50-60°C.

PROCESSING CONSIDERATIONS

Processing considerations are dictated by a desire for maximum reliability and minimum maintenance. All maintenance must be done by remote control and by use of overhead cranes and master-slave manipulators. The goal is to have a process that can be counted on to operate around the clock for 270-300 days out of each year.

Processing considerations which help attain this goal include:

- . Operate equipment under negative pressure
- . Avoid close tolerances (mechanical or chemical)
- . Minimize moving parts
- . Minimize use of manipulators

It is standard radiochemical processing practice to maintain vessels and operating equipment under a slight negative pressure with respect to the cell. This helps maintain control of radioactivity in the cell and prolong the life of radiation sensitive items such as manipulator boots and electrical cables. Close mechanical tolerances are avoided to facilitate remote maintenance wherever possible. Likewise chemical tolerances should be broad. This reduces the need for costly radiochemical analysis and critical process control. Moving parts are minimized since moving parts generally mean wear and more frequent maintenance. Likewise manipulator use should be minimized. Manipulators have to be changed out and repaired frequently and can become a major maintenance item.

STATE-OF-THE-ART IN HLW GLASS PROCESSING

Because of the foregoing considerations the waste glass processes which have evolved from the R&D conducted in many countries over the past 20 years share important common characteristics, including:

- . Simplicity

- . Product is relatively low-melting glass
- . Waste loading is 20-40 wt%.

Many of the waste glass-making processes are quite well developed and are candidates for commercial use. I will describe only two, developed in the U.S., but good descriptions of the others can be found in TAD (3) and in the proceedings of the 1976 Vienna symposium on management of radioactive wastes (4).

1. Spray Calcination/In-Can Melting (5)

Spray calcination/in-can melting is a process developed at ERDA's Pacific Northwest Laboratory (PNL) specifically for the vitrification of commercial high-level waste. It is a close-coupled tandem process in which the liquid waste is first dried and denitrated, and then combined with glass frit and melted. The solidification equipment is shown in Figure 4.

The spray calciner operates with a wall temperature of 700°C. The HLLW is atomized into the top of the calciner and as the droplets fall through the heated chamber all of the water is evaporated and most of the nitrate decomposed to give a very fine high surface area powder. The powder either falls directly into the close-coupled melter, or collects on the sintered stainless steel filters from which it is blown back into the melter periodically.

Specially-formulated glass frit is metered into the melter at a predetermined rate. The frit reacts with the calcine in the melter, which is held at 1050°C, to form a low-melting glass in which almost all of the waste constituents are dissolved. Ray Turcotte will discuss the microstructure of the glass and the solubility experiments in his paper later.

The spray calcination/in-can melting process is a simple process with few moving parts. Its major feature is that the glass is melted in situ in the canister, obviating the necessity for transfer of molten glass between melter and canister. Because the melting is done in the steel canister, only low-melting glass formulations can be used.

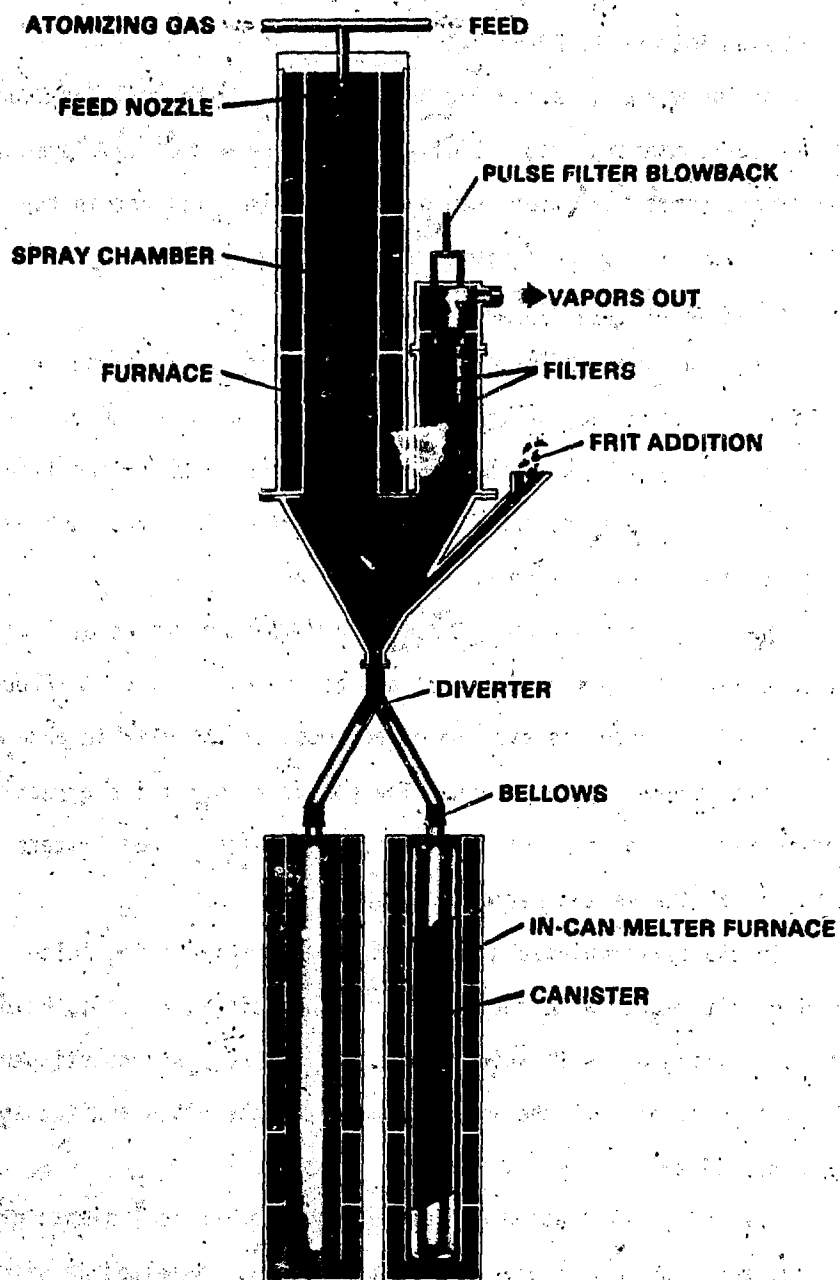


Figure 4. Spray Calcination/In-Can Melting

2. Continuous Ceramic Melting (6)

A continuous ceramic melter process is also under development at PNL which makes glass by a process closely allied with commercial electric glass melter processes, although on a smaller scale. Use of the electric melter permits a large amount of flexibility. Different kinds of waste calciners can be coupled to the melter and it is even possible to feed liquid waste directly to the melter. Since the melter is constructed of refractory bricks the use of higher melting glass formulations is possible. The molten glass can be cast in large canisters to yield a product similar to that from the SC/ICM, but it can also be cast in smaller shapes if desired, or even made into marbles.

A current PNL design for a continuous ceramic melter is shown in Figure 6. Power is supplied by current conducted directly through the molten glass between electrodes submerged in the melt. Several startup techniques are available for initially melting the glass before the submerged power electrodes are turned on. An important feature of this melting concept is that once the melter is operating the surface of the melt can be relatively cool, in fact a "cold cap" of unmelted calcine can be maintained to act as a filter for trapping volatiles.

An aspect of ceramic melting still under development is the transfer of glass out of the melter into the canister. Several types of valves have been tested in Europe and the U.S. The PNL design shown in Figure 5 features a tilt drain concept which will be tested in the next few months.

TRENDS IN FUTURE PROCESSING DEVELOPMENT

There is continuing activity in the field of HLW solidification process development. The newer development activity is marked by a trend toward making the solidified product in smaller pieces which are then combined in a standard-sized canister, usually with a metal matrix for increased thermal conductivity. There are different reasons for the trend to smaller pieces. Glass-ceramics, for instance, can require closely controlled thermal cycling which can't be done in massive

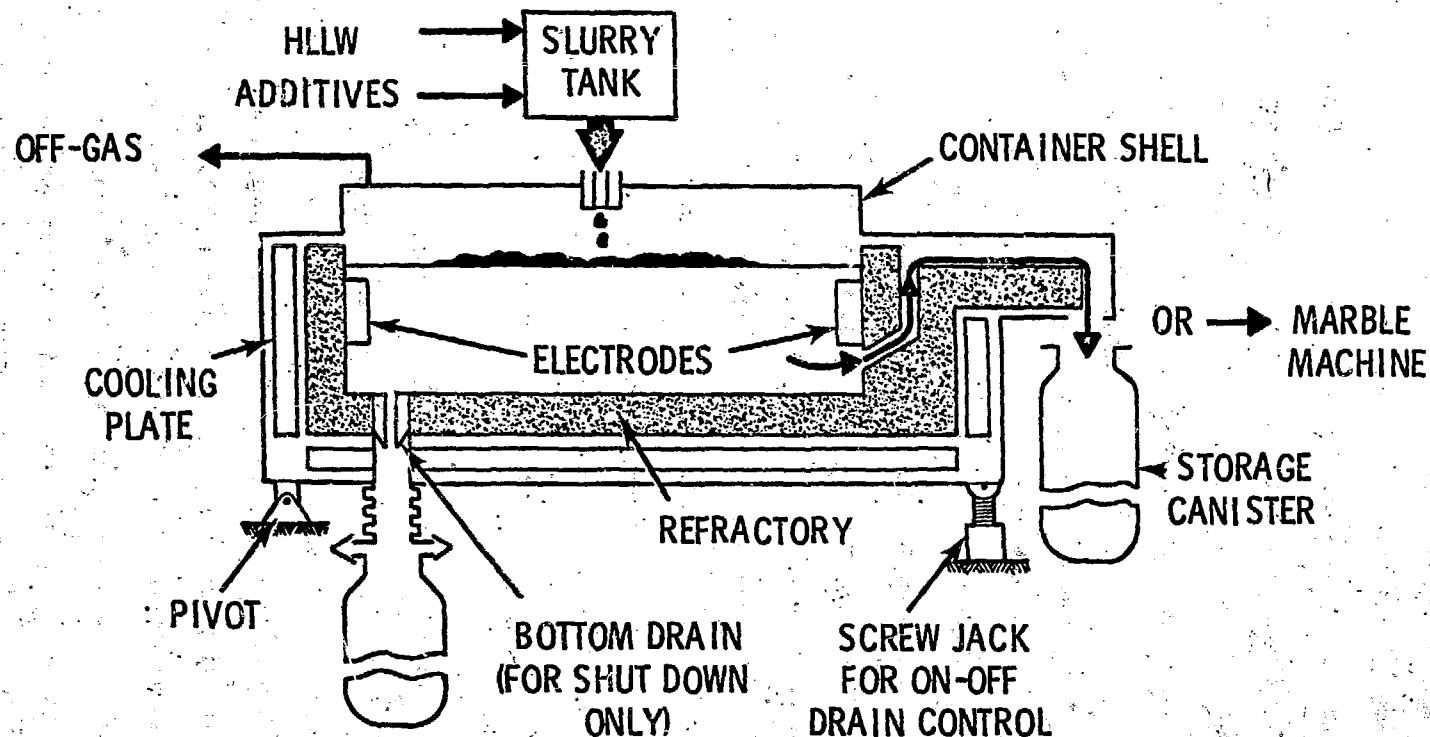


Figure 5. Liquid Fed Continuous Melter Vitrification Process

canisters of self-heating glass, but only with smaller pieces. Smaller pieces also permit more thorough and direct quality control, it being possible to inspect each piece individually before packaging in the storage canister, if desired.

I will describe just two of the potential future processes. Again more information on other processes can be found in references 4 and 5. Both of these future processes can utilize a glass waste form. The second process can also utilize crystalline ceramic waste forms.

It is evident that these processes are more complex than the state-of-the-art glass processes. Their adaption will depend on assessments of the trade-off between the penalties imposed by process complexity and the benefits gained by potentially improved products.

1. Pamela Process

The Pamela process is being developed by the German Gelsenberg company of Julich, Germany, in cooperation with Eurochemic at Mol, Belgium. The process is shown schematically in Figure 6.

The first step in the Pamela process is the manufacture of a phosphate waste glass in an electric melter using tin oxide electrodes. Phosphate glass can be made by an all-liquid process. A calciner is not required.

A major problem with phosphate glass is the extreme corrosivity of the melt. Thus the bead-making crucible is platinum. The crucible has a series of orifices at the bottom and by proper control of temperature, and thus viscosity, the low-melting phosphate glass will break into droplets as it drains from the orifices. The droplets are quenched to form glass beads about 1/8 - 1/4-inch diameter on the rotating steel disk. They are scraped from the disk into a hopper from which they are transferred to the bottom of a canister filled with molten lead.

The final product is a canister filled with small phosphate glass beads in a lead matrix. The process is designed to maintain the solidified phosphate glass below 400°C at all times. Devitrification begins at about 500°C and devitrification degrades phosphate glass considerably. The leach rate is increased by a factor of 1000.

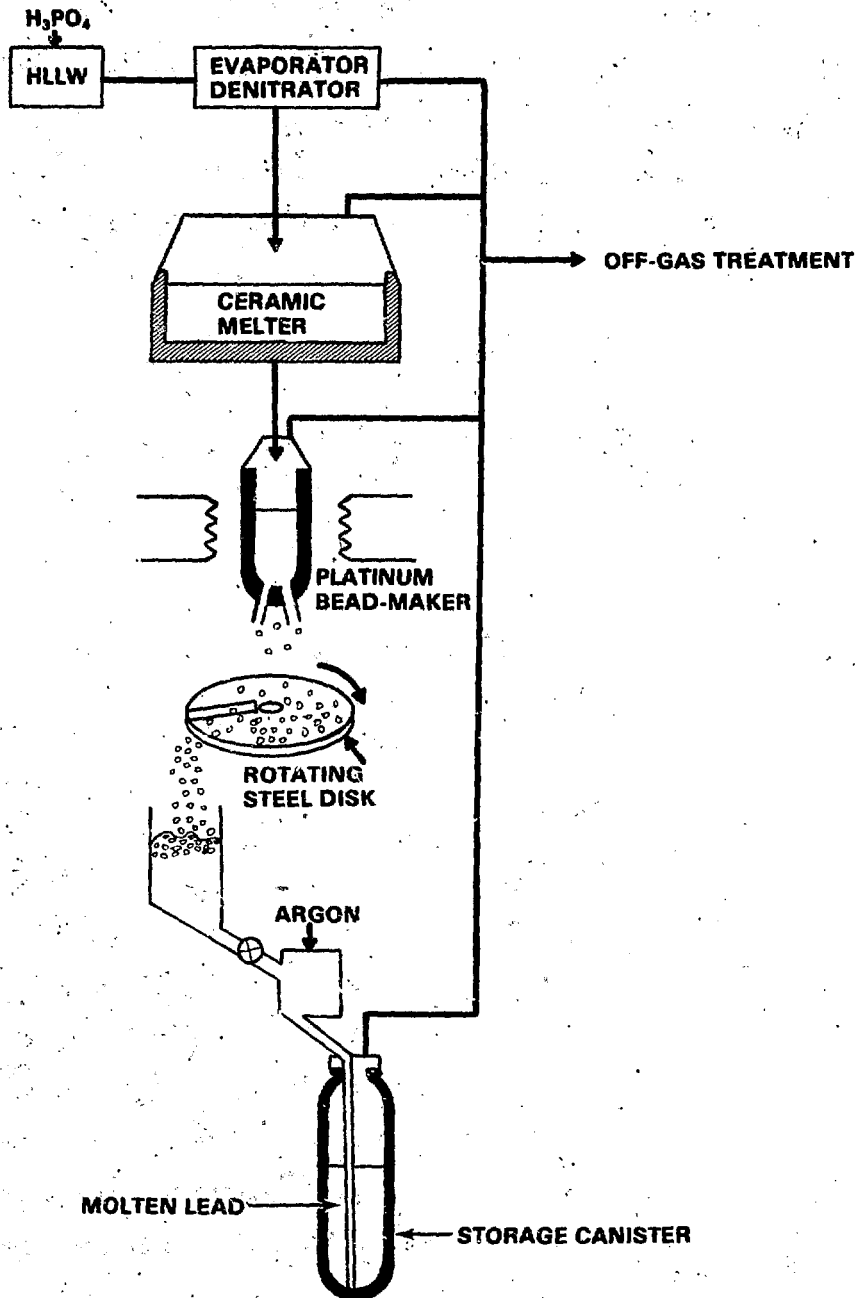


Figure 6. The Pamela Process

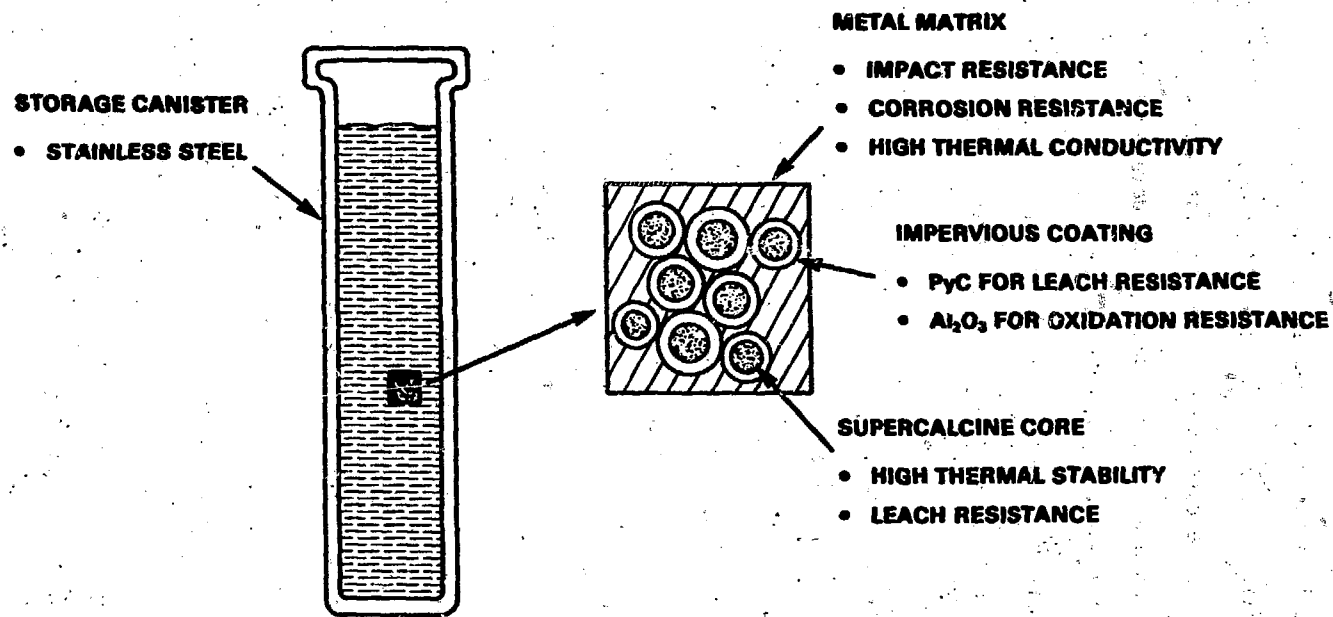


Figure 7. Multibarrier HLW Concept

2. Multibarrier Process

The multibarrier process is possibly more correctly identified as a concept at this time. It is being developed at PNL and one version is shown in Figure 7.

This concept also begins with small pieces of solidified waste, designated the core material. The core material can be glass beads, or pellets of crystalline ceramic material, such as "supercalcine" being developed by Dr. McCarthy at Penn State, which he will describe in more detail later.

The differentiating feature of the multibarrier process is the inert coating which is placed around each pellet of core material. The inert coating can be material with known durability in the environment, such as Al_2O_3 or SiO_2 . Characterization of the quality of the waste form then depends primarily on assessing the porosity, adherence, and other properties of the coatings, a relatively simple task compared to fully characterizing the complex primary waste core particles.

Currently CVD techniques appear most promising for applying the coatings. Precoats can be applied as in the example shown in Figure 7. Radiation effects have not been studied yet but it is expected that because of the small size of the particles relatively large differences in radiation-induced swelling or shrinking can be accommodated.

The final step in the process is to embed the coated particles in a metal matrix in a large canister. The metal matrix imparts increased thermal conductivity and impact resistance to the total waste form.

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PROPERTIES AND CHARACTERISTICS OF HIGH-LEVEL WASTE GLASS*

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In reviewing the properties and characteristics of high-level waste glass, three important characteristics can be noted which have contributed to the choice of glass as the first line waste form--these are: 1) Low leachability, 2) the ability of glass to incorporate a wide variety of elements, and 3) the large size-low surface area solid which can be formed. These properties are in addition to the ease with which the glass waste form can be produced.

The important properties and characteristics of a waste form are shown in the characterization matrix in Figure 1. In this paper, the composition of wastes and glasses will first be reviewed. Second, anticipated thermal environments for waste glasses from processing, interim storage, transportation, and final disposal will be covered in more detail than the preceding paper. After which, the dependent variables of environmental reactions, volatility, bulk properties, and finally, physical strength will be covered in that order.

WASTE COMPOSITION

High-level waste is composed of elements from three sources: fission products are produced from burnup of the fuel in reactor and represent over 99% of the radioactivity in all nuclear wastes; second, actinides which result from neutron capture and uranium and plutonium that have not been completely removed during solvent extraction in the reprocessing plant, (typically 0.5 - 1.0 wt%); and third, nonradioactive chemicals

* Work performed under ERDA Contract EY-76-C-06-1830

REFERENCE MATRIX FOR WASTE FORM CHARACTERIZATION

DEPENDENT VARIABLES			INDEPENDENT VARIABLES		INFORMATION NECESSARY TO DEFINE SOURCE TERM																					
					COMPOSITION & RADIATION DOSE		TEMPERATURE, TIME AND ENVIRONMENT																			
					FORMULATION		PROCESSING CONDITIONS		STORAGE AND TRANSPORT CONDITIONS		ACCIDENT CONDITIONS		DISPOSAL CONDITIONS													
					RADIOACTIVE INVENTORY	WASTE FROM RADIOACTIVE CONSTITUENTS OF WASTE	ADDITIVE COMPOSITION	ADDITIVE WASTE RATIO	PROCESS EQUIPMENT	MATERIAL OF CONSTRUCTION	TEMPERATURE	TIME AT TEMPERATURE	RATE OF COOLING	AGITATION (WHERE APPLICABLE)	CANISTER MATERIAL	COOLING MEDIUM	THERMAL HISTORY	TIME	TEMPERATURE TRANSIENTS	IMPACT ENERGY	SURROUNDING MEDIA	TIME IN CONTACT WITH MEDIA	TIME	THERMAL HISTORY	STORAGE MEDIUM	AT CONTACT
PROPERTIES OF WASTE FORM AFFECTING POTENTIAL FOR DISPERSION OF CONTAINED RADIOACTIVITY VIA AIR OR WATER	ENVIRONMENTAL REACTIONS	CORROSION OF CONTAINMENT (EXTERNAL)																								
		CORROSION OF CONTAINMENT (INTERNAL)																								
		LEACHABILITY (STATIC SYSTEM)																								
		LEACHABILITY (DYNAMIC SYSTEM)																								
		VOLATILITY																								
	THERMAL STABILITY	PHASE CHARACTERIZATION																								
		DEVITRIFICATION (WHERE APPLICABLE)																								
		RADOLYTIC GAS FORMATION																								
		HELIUM SOLUBILITY AND PERMEABILITY																								
		RADIATION DAMAGE																								
	RADIATION EFFECTS (1)	DENSITY																								
		THERMAL CONDUCTIVITY																								
		VISCOSITY (WHERE APPLICABLE)																								
		THERMAL EXPANSION COEFF.																								
		ELECTRICAL CONDUCTIVITY (WHERE APPLICABLE)																								
	BULK PROPERTIES	FRAGILITY, MECHANICAL SHOCK																								
		FRAGILITY, THERMAL SHOCK																								
		INDUCED STRESSES (DEGREE OF ANNEALING)																								

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

Figure 1. Reference Matrix for Waste Form Characterization

added during reprocessing such as gadolinium for criticality control and addition of the intermediate level waste stream from clean-up of the solvent extraction solutions which add sodium and phosphate. Various elements and sources are shown in Figure 2. Additional detail can be found in Reference No. 1. As can be seen, the wastes contain a wide variety of elements with a wide variation of chemical behavior. A waste form must be able to contain each of these elements in a stable solid.

The waste compositions from reprocessors are changing as designs and regulations are formulated. One example of this is shown in Figure 3 where Na, Fe, and Gd content of an early, interim and current waste composition for the AGNS (Allied General Nuclear Services) plant in Barnwell, South Carolina, is noted. The early composition was used for glass development about three years ago, then the interim replaced it with lower levels of Na and Fe, however, the addition of Gd was required. The current composition with its very high levels of Gd has resulted from a change in requirements for Gd concentration in the dissolver. The important thing to note is that compositions of a waste are changeable and a waste form must tolerate these changes without serious effects on its properties.

GLASS COMPOSITION

Two typical waste glass compositions for solidification of HLW are shown in Figure 4 along with commercial "Pyrex" glass. Comparisons of the compositions show several major differences. Waste glasses with the need for high waste concentrations are low in silica. They also have additional alkali and alkaline earths to lower their processing temperatures. Waste glasses are typically melted at temperatures of 1050 - 1150°C whereas the commercial glasses are more typically melted at ~1600°C. The zinc borosilicate glass 72-68 was developed early in the waste fixation program and has been extensively characterized and most of the data in both this paper and the following paper were obtained with this composition.

As described above, one of the important characteristics of waste glasses is that they must tolerate wide variations in waste content and composition. The AGNS 76-183

ELEMENTS IN HIGH-LEVEL WASTE

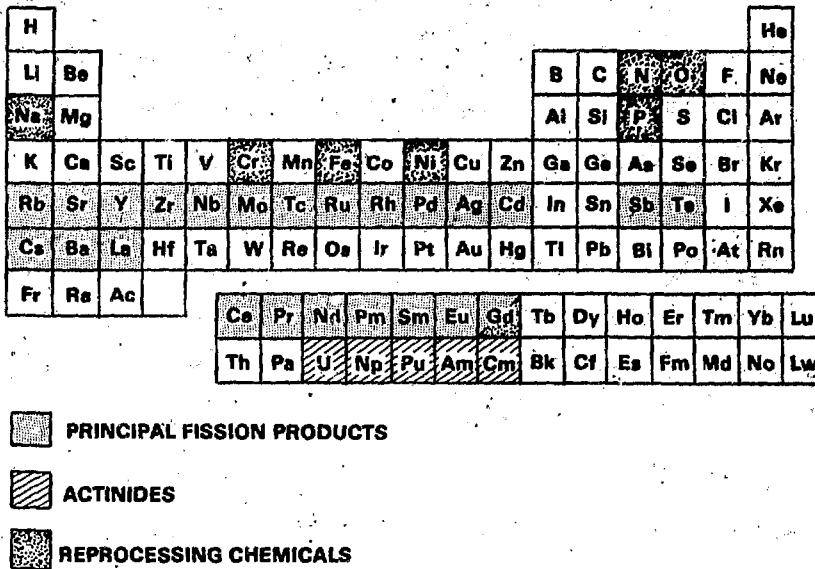


Figure 2. Source of Elements in High-Level Wastes

CHANGES IN WASTE COMPOSITIONS

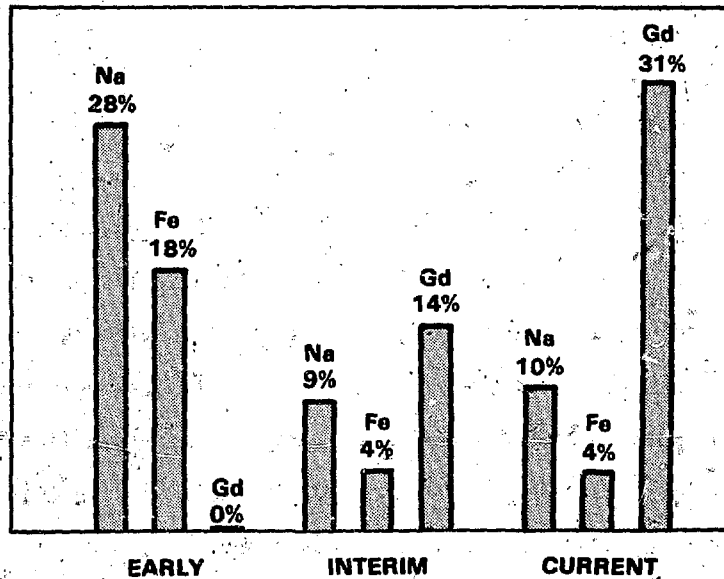


Figure 3. Changes in Projected Waste Composition from the AGNS, Barnwell, South Carolina, Reprocessing Plant During the Past four years.

TYPICAL GLASS COMPOSITIONS

	ZINC BOROSILICATE 72-68	INTERIM AGNS 76-183	PYREX 7740
SiO ₂	27.3	35.5	80.5
TiO ₂	—	6.0	—
Al ₂ O ₃	—	1.0	2.2
B ₂ O ₃	11.1	9.5	12.9
ZnO	21.3	—	—
CuO	—	3.0	—
Na ₂ O + K ₂ O	8.1	10.0	4.2
MgO + CaO + SrO + BaO	5.9	2.0	—
WASTE	26.3%(PW-4b)	33%(PW-7a)	—

Figure 4. Compositions of Typical High-Level Waste Glasses Compared to a Durable Commercial Glass.

EFFECT OF WASTE CONTENT

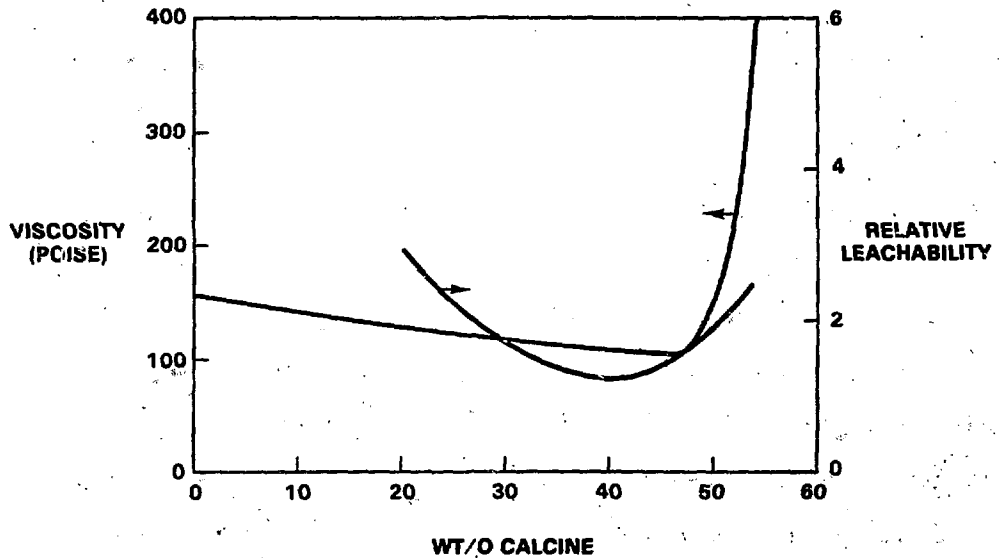


Figure 5. Plot Showing Minor Changes in Viscosity and Leachability of a 76-183 Type Glass with Changes in Waste Content.

glass is a waste glass that has demonstrated this characteristic. While the reference concentration of waste is 33 wt%, tests have been run on leachability and viscosity with samples containing from zero to 54 wt% waste. As can be seen in Figure 5, viscosity is below the 200 poise upper limit for melting with up to near 50 wt% waste. Also, leachability does not change more than a factor of two which is a minor change. It can be noted, then, that glass does have the potential of accepting a wide range of waste compositions.

ANTICIPATED THERMAL ENVIRONMENTS

As pointed out by John Mendel earlier, the thermal power of the waste decreases quite rapidly with time. To allow a better feeling for the anticipated temperatures in the glass from the decay heating, Figure 6 was constructed. It shows what the ΔT from surface to centerline would be in a 12 in. diameter casting of typical waste glass as a function of time since the fuel left reactor. As can be noted, with no fins in the canister, a ΔT of $\sim 500^\circ\text{C}$ would exist between canister surface and centerline if the waste was solidified at two years out of reactor. With the ten years allowed before transfer of the waste to the reposition, the ΔT would decrease to near 100°C and after about 100 years, only a minor temperature gradient would exist in the waste. This also implies that any thermal effects will most likely occur during the first 10 years and definitely in the first 100 years.

Our current canister design calls for the use of a finned canister for in-can melting. The fins double the effective thermal conductivity of the glass and would reduce the temperatures in Figure 6 by a factor of 2.

With the anticipated ΔT 's and appropriate surface temperatures, Figure 7 was determined. The melting conditions for in-can melting will typically be 1050°C with a multizone furnace to allow control of surface temperature. After a zone is melted, the surface will be molded, however, centerline temperatures may be allowed to rise to 1150°C . After the canister is filled, it will be removed from the furnace and may be handled hanging in air. This will produce a surface temperature of $350 - 400^\circ\text{C}$ for a

GLASS DIFFERENTIAL TEMPERATURES

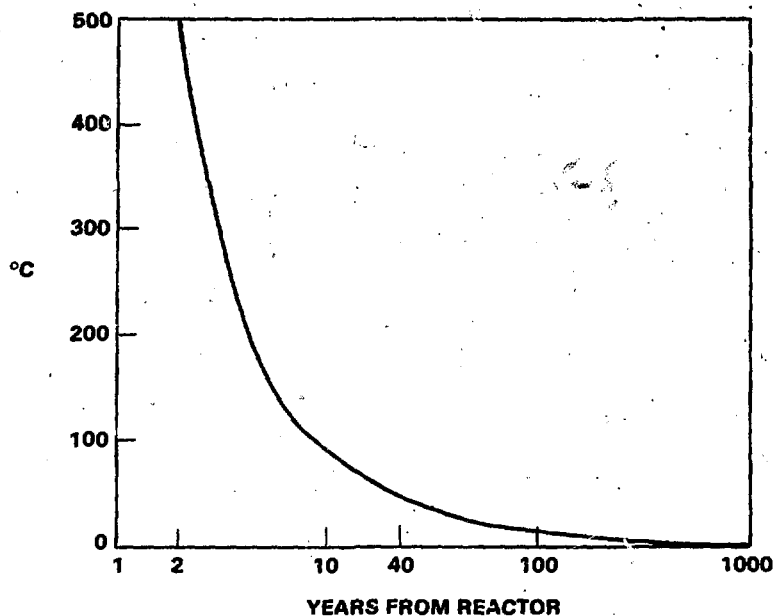


Figure 6. Difference in Centerline and Surface Temperature of a 12-inch Diameter Unfinned Canister of High-Level Waste Glass as a Function of Time

ANTICIPATED TEMPERATURES FOR WASTE GLASSES

	<u>SURFACE</u>	<u>CENTERLINE</u>
MELTING	1050°C	1150°C
HANDLING	350-400°	550-800°
BACIN STORAGE	50°	150-500°
TRANSPORTATION	100-350°	200-450°
ACCIDENTS	500-800°	600-900°
DISPOSAL	30-250°	30-350°

Figure 7. Anticipated Temperatures for High-Level Waste Glasses During Various Stages

two-year old waste. If finned, a centerline temperature of about 550°C will be reached and if unfinned, about 800°C. After welding, inspecting and testing, the canister will be transferred to a water storage basin for interim storage for up to ten years. Water basins are typically in the 40-60°C range and initial temperatures near the centerline of ~500°C are anticipated for unfinned cans. With age, the centerline temperature would decrease to near 150°C. The canisters are then loaded into a shipping cask for transportation to the ultimate disposal site. Casks can be either static cooled or force cooled with a corresponding difference in temperature. Transportation may offer the greatest potential for an accident with a subsequent hydrocarbon fire. Fire temperatures are typically <800°C, and due to their normally short duration, waste temperatures would probably not exceed the fire temperature. At the disposal site which is currently viewed as a salt formation, temperatures will be limited to 250°C from the salt-canister surface and will decay slowly over a long period to ambient temperatures. Centerline temperatures would also continue cooling to ambient.

From this review, it can be noted that the two most likely periods for devitrification to occur are during initial handling and during an extreme accident when other factors may be more important. At other times, the total glass will be below the transition temperature where crystal growth would be expected to be very slow.

CORROSION AND LEACHABILITY

The 1050°C melting temperature is well above the normal use temperatures for the current reference canister material--304L stainless steel. At the melting temperature, some concern exists about the attack of the molten glass on the canister. The data has been determined for a series of temperatures (2) with the 72-68 glass and is shown in Figure 8. With the typical 1050°C melting temperature, a corrosion rate of ~40 mm/yr was measured. When this is converted to a 16-24 hour cycle for a canister in the furnace, it can be seen that corrosion of the canister will only be about 0.1 mm.

One of the prime reasons for making a glass is that waste glasses can be formulated

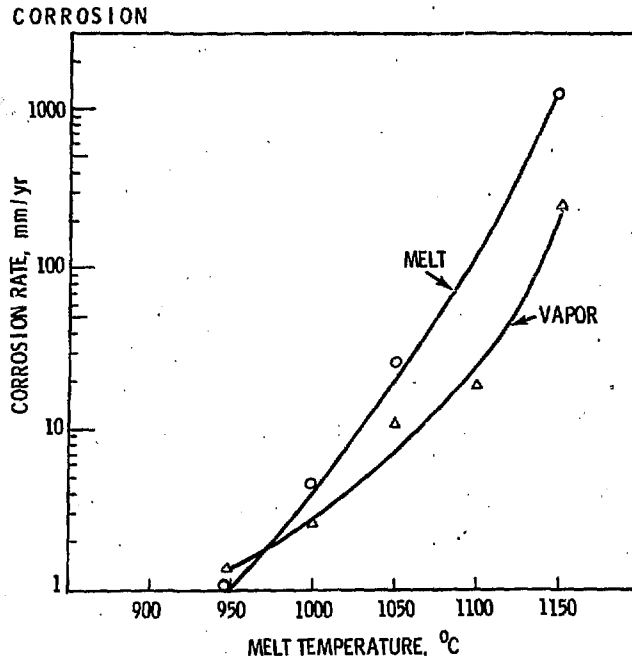


Figure 8. Corrosion of 304L Stainless Steel by a 72-68 Zinc Borosilicate Waste Glass

COMPARATIVE CHEMICAL DURABILITIES

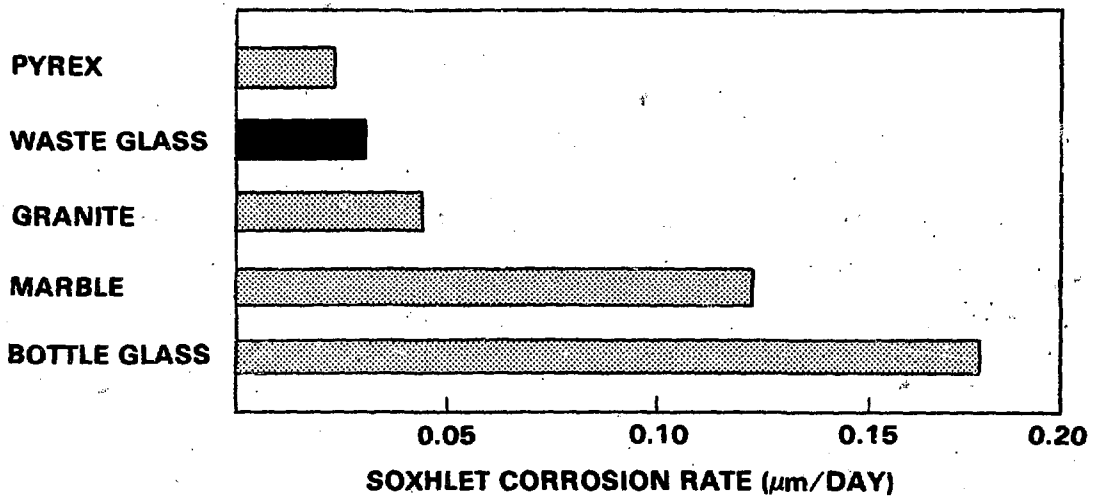


Figure 9. Comparison of Corrosion Rates of Waste Glass and Other Durable Materials in a 99°C, Distilled Water Soxhlet Test

which have very low leach rates. This is shown in Figure 9 where the leach or corrosion rate of various materials is compared. The tests were performed in a Soxhlet type apparatus which operates at 99°C with continuous reflux of distilled water. This test ranks the waste glass near Pyrex and similar stable materials such as granite and marble found in nature. This comparison indicates that it is unlikely that much further improvement in leach resistance can be made for a homogeneous waste form.

Leach rates are a function of many things including, time, temperature, sample form, solution pH, leachant replenishment rate, past thermal history, and compositions. The effect of time is shown in Figure 10. This test has been in progress for nearly a year. Cesium concentrations of the leach solution are determined and then converted to a bulk leach rate. As can be noted, the leach rates have dropped nearly an order of magnitude during the testing period.

Devitrification of a waste glass is not desirable, but is not catastrophic. As can be seen in Figure 11, Soxhlet leach rates increase nearly an order of magnitude for sample devitrified at 700°C, the temperature of maximum devitrification for the zinc-boro-silicate waste glass. Samples for this test were held at the respective temperatures for two months before leach testing. The change in leach rate due to thermal effects is the major change identified in waste glasses.

VOLATILITY

At higher temperatures, it is possible to vaporize some of the waste and glass constituents (3). The results of a four-hour vaporization test are shown in Figure 12. Two things can be noted from this data. First, the total vaporization rate is linear in the $\ln Q$ vs $1/T$ plot indicating that the total vaporized will increase rapidly with temperature. This is one reason that process temperatures should be kept below 1200°C. It also indicates that volatility will only be important during processing. The second point is that cesium is the most volatile species and also one of the most toxic so its volatility should be given the greatest consideration.

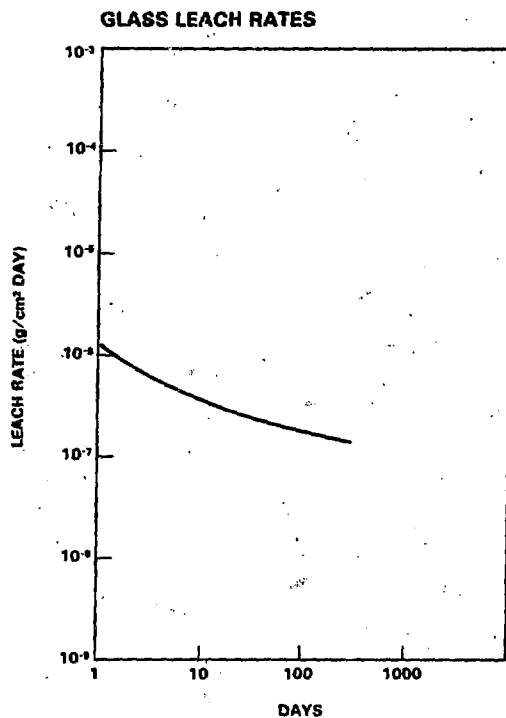


Figure 10. Bulk Leach Rate of a 72-68 Glass Based on Cesium

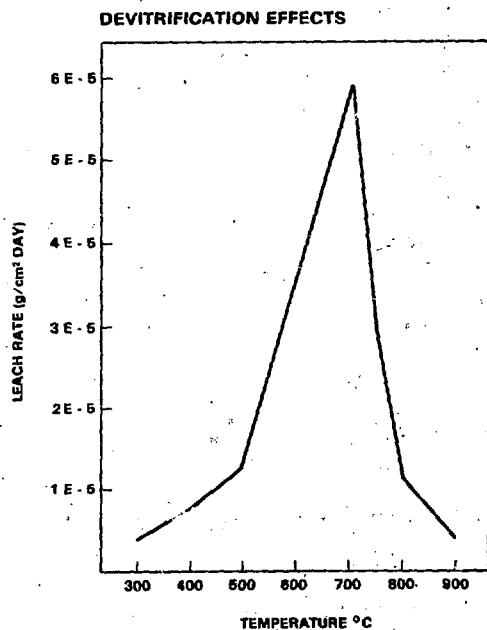


Figure 11. The Bulk Leach Rate (as Determined by the Soxhlet Method) of Waste Glass 72-68 after Two Months at Temperature

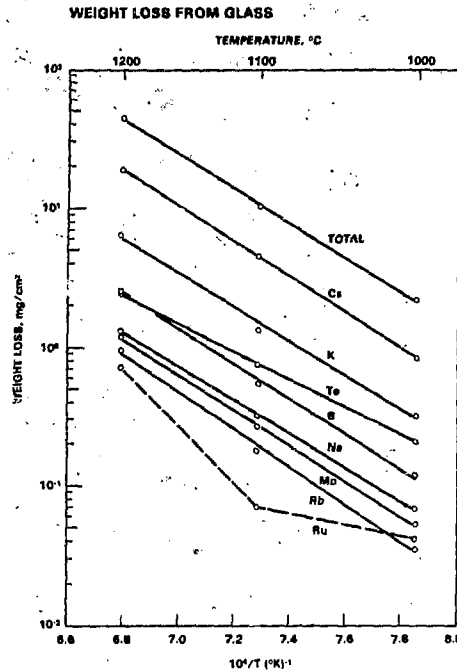


Figure 12. Volatile Losses from a 72-68 Type Glass in Four hours

BULK PROPERTIES

- DENSITY - 3.0 - 3.7 g/cc
- THERMAL CONDUCTIVITY - 0.83 - 1.2 WATTS/m•K
- VISCOSITY - <200 POISE
- SOFTENING POINT - 550 - 600°C
- EXPANSION COEFFICIENT - 80 - 90 X 10⁻⁷/°C
- ELECTRICAL CONDUCTIVITY - <1 mho

Figure 13. Bulk Properties of Typical High-Level Waste Glasses

**1/2 SCALE CANISTER-30 FOOT EDGE-ON
DROP ONTO CONCRETE**

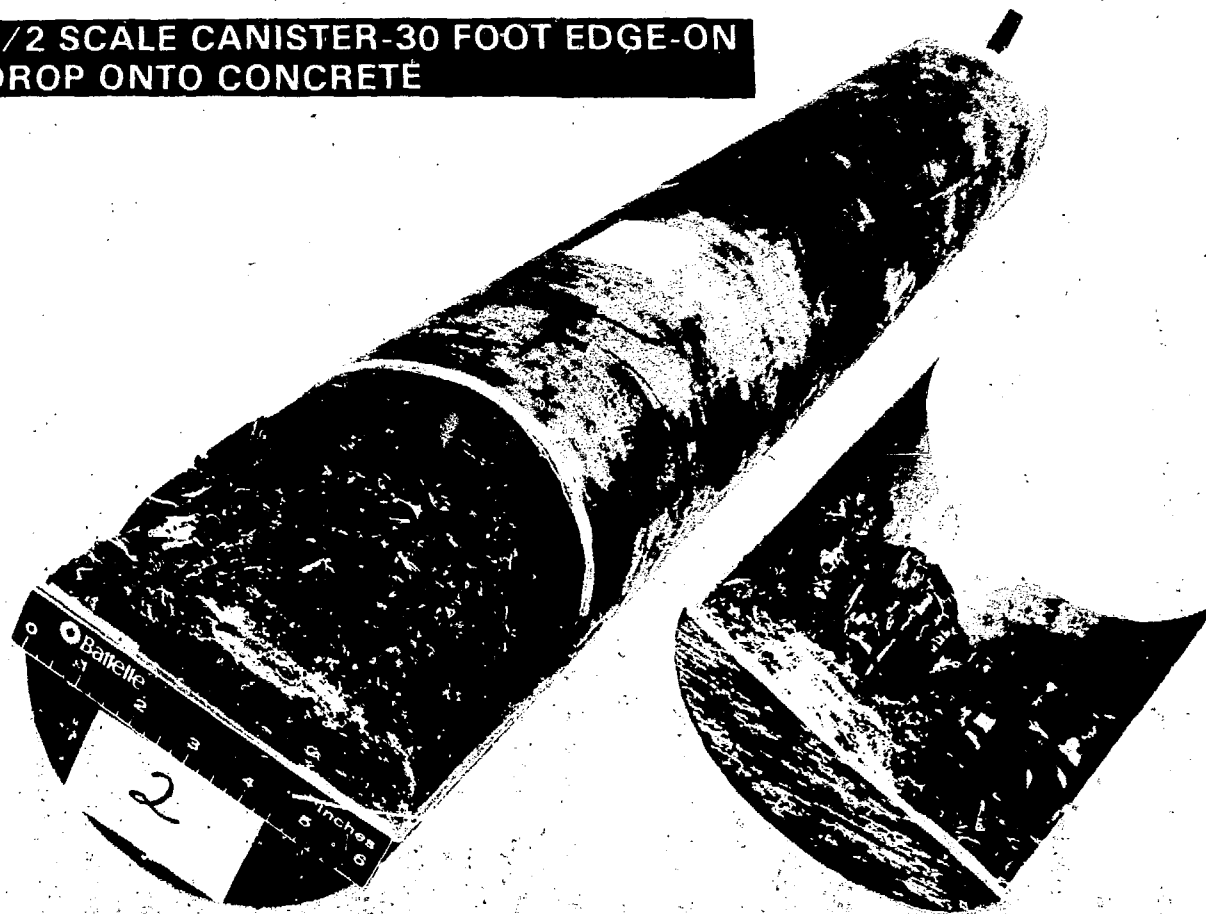


Figure 14. A One-Half Scale Canister of Simulated Waste Glass After Impact and Sectioning of the Canister.

PHYSICAL STRENGTH

The strength of glass is typically not a strong function of composition, but is controlled more by imperfection of the surface or residual stresses. Of most importance to waste containment is the surface area of the waste form. This can be shown by the equation

$$\text{Quantity leached} = \text{leach rate} \times \text{surface area} \times \text{time}.$$

From the equation, it can be noted that surface area reduction is just as important as leach rate reduction. Since glass is melted and cast, it has the potential of having a much lower surface area than powders which are sintered and still contain interconnected porosity. It is also possible to cast the glass into large pieces. The two concerns then become resistant to impact damage and thermal shock.

A series of tests were run on one-half and one-sixth scale canister with impact velocities of up to 80 miles/hr. (4). After impact, the canisters were opened and the particle size of the glass was determined. Figure 14 shows one of the one-half scale canisters that was dropped 30 ft on to a concrete foundation to impact the lower canister corner. It can be noted that a relatively small part of the glass was fractured in this sample. The canister was not ruptured by the impact and so even the small fraction of fine particles could not be dispersed. The increase in surface area for all of the samples was calculated and is shown in Figure 15. The canister in Figure 14 had an increase in surface area of about one (1) or was double that of the original monolithic piece of glass.

It is likely that the glass castings within the canister will be thermally shocked during the cooling process. To determine how important this might be, a set of one-half scale canisters was cooled at different rates. The results in Figure 16 show that for a canister which is removed directly from the furnace after melting and allowed to air cool, the cracking will increase the surface area about a factor of 10. This low value occurs since the exterior surface acts as insulation to the interior material and allows it to cool more slowly, thus it is less cracked. One way to avoid

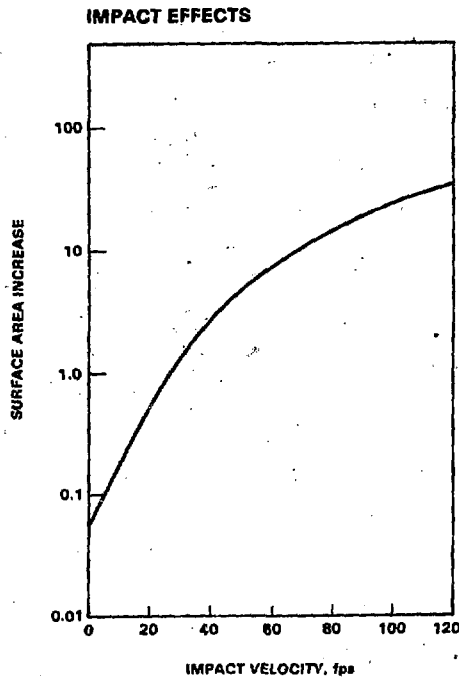


Figure 15. The Fractional Increase in Surface Area of Canisters of Simulated HLW Glass after Impact

THERMAL SHOCK

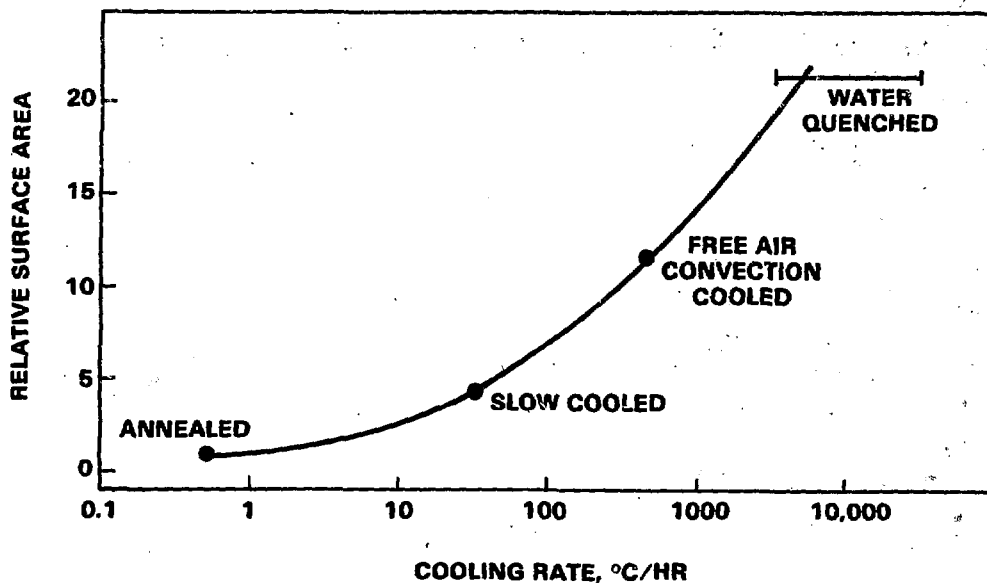


Figure 16. The Increase in Surface Area of a 6 in. Diameter Canister of Simulated HLW Glass after Thermal Shock

thermal fracture is to make smaller glass shapes; however, to make a glass shape which can be cooled directly in air would limit the size to about 1/4 inch. If the surface area of the equivalent volume of material is then calculated, it is much greater than the factor of 10 produced by thermal shock. Forming smaller glass shapes would also greatly complicate the process.

SUMMARY

This paper has briefly reviewed many of the characteristics and properties of high-level waste glasses. From this review, it can be noted that glass has many desirable properties for solidification of high-level wastes. The most important of these include:

- Low leach rate.
- The ability to tolerate large changes in waste composition.
- Tolerance of anticipated storage temperatures.
- A low surface area even after thermal shock or impact.

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PHASE BEHAVIOR AND RADIATION EFFECTS IN HIGH LEVEL WASTE GLASS*

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INTRODUCTION

Although as-prepared waste glasses have favorable chemical and physical properties, it is well recognized that the influence of long-term self-heating and radiation damage must be understood with respect to the rate and magnitude of any changes. Detailed studies of selected glasses in these two areas are therefore major parts of the overall characterization program. These studies are undertaken primarily on simulated, nonradioactive glasses (doped with 1 wt.% ^{244}Cm for radiation damage work), with the intention of establishing a direct correlation to behavior of actual fuel level waste glasses, as they become available. The first fully radioactive HLW glass of the 72-68 composition, which is now being examined, does not appear to behave differently than expected from the studies summarized here using stand-in materials.

Within the scope of this paper, only some aspects of on-going and past work can be covered. Several reports have been published containing much more experimental and technical detail than discussed here. These include a review paper by Mendel et al (1), a study of stored energy by Roberts, Jenks and Bopp (2), helium diffusivity measurements by Turcotte (3), and devitrification studies by Turcotte and Wald (4).

PHASE BEHAVIOR

The phase characterization work is outlined in Figure 1 and is accomplished through optical and scanning electron microscopy, microprobe analysis, and

* Work performed under ERDA Contract No. EY-76-C-06-1830.

quantitative x-ray diffraction analysis. The as-prepared glasses frequently contain small concentrations of glass insoluble phases such as RuO_2 and Pd and sometimes refractory oxide phases such as CeO_2 or spinel phases $(\text{Fe}, \text{Cr}, \text{Ni}, \text{Zn})_3\text{O}_4$ are also present. With appropriate thermal treatment, other phases may appear which are characterized with respect to stoichiometry, crystal structure, and concentration as a function of time and temperature. Changes in macrostructure such as cracking or settling of dense phases as a result of devitrification are evaluated.

NUCLEAR WASTE GLASS PHASE CHARACTERIZATION

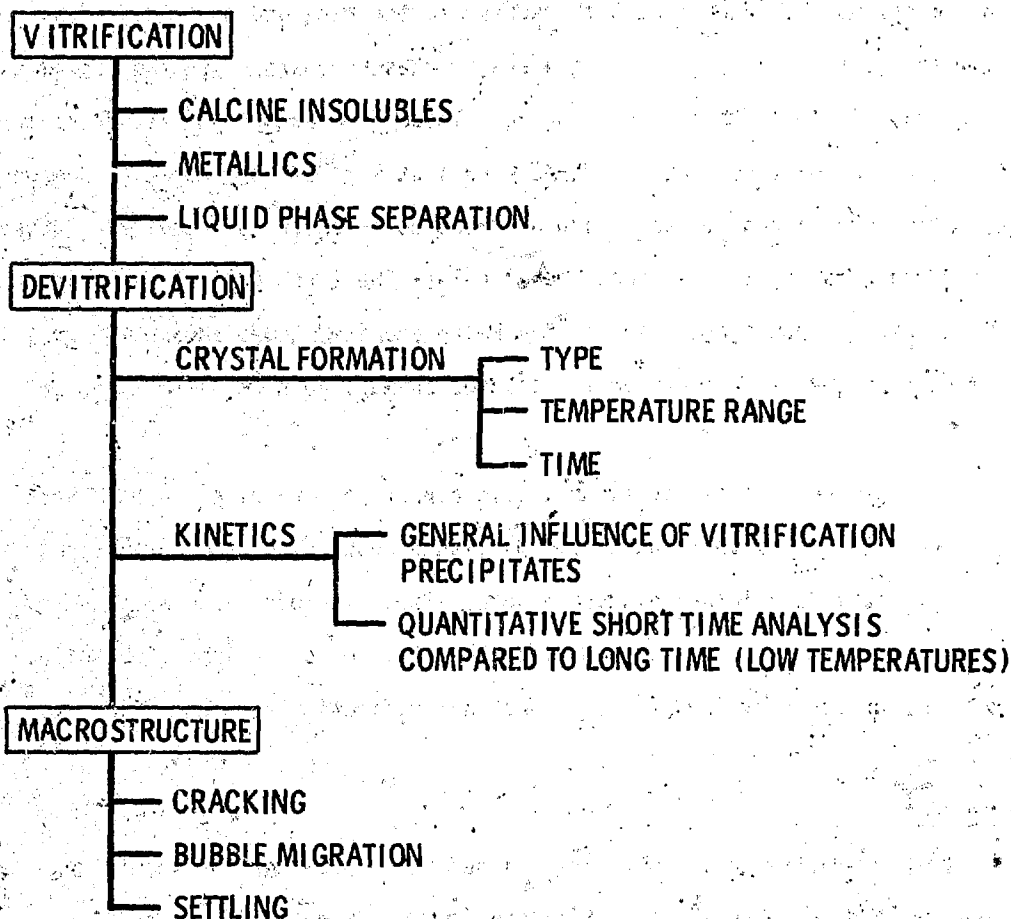


Figure 1. Phase Behavior Program Outline

Tables 1 and 2 show the glass composition and the annealing schedule used in the present work, for which data are now available through one year of annealing. More detailed kinetic studies have generated a large number of data for times less than one week. Table 3 lists the observed phases in 72-68 glass and maximum concentrations achieved after one-year anneals. The major devitrification products are Zr_2SiO_4 , $(\text{Ca}_{0.25}\text{Sr}_{0.5}\text{Ba}_{0.25})\text{MoO}_4$, and an apatite phase, $\text{Ca}_2(\text{RE}^{3+})_8(\text{SiO}_4)_6$. Typical x-ray fluorescence maps of a devitrified glass are shown in Figure 2, where the various elemental concentrations are clear. Figure 3 shows typical x-ray diffraction traces of as-prepared and devitrified glasses. With the exception of one very small peak, all of the diffraction patterns can be accounted for. The 'vitreous' and devitrified XRD traces have not been normalized; both samples contain 1.4 wt.% RuO_2 as a point of reference.

Table 1
COMPOSITION OF WASTE GLASS USED FOR CHARACTERIZATION
OF THERMAL AND RADIATION EFFECTS

SiO_2	27.31 wt%	N_2O	0.66 wt%	TcO_2	0.46 wt%
B_2O_3	11.15	P_2O_5	0.42	Cs_2O	1.82
Na_2O	4.06	Rb_2O	0.22	La_2O_3	0.93
K_2O	4.06	Y_2O_3	0.38	CeO_2	2.11
ZnO	21.34	ZrO_2	3.13	Pr_6O_{11}	0.94
CaO	1.47	MoO_3	4.03	Nd_2O_3	2.95
MgO	1.47	RuO_2	1.88	Sm_2O_3	0.58
SrO	2.15	Rh_2O_3	0.30	Eu_2O_3	0.13
BaO	2.47	PdO	0.94	Gd_2O_3	0.09
Fe_2O_3	0.95	Ag_2O	0.06	UO_2	1.26
Cr_2O_3	0.22	CdO	0.06		

Table 2

THERMAL TREATMENTS FOR THERMAL EFFECT STUDIES

Temperature (°C)	Time					
	2 hours	1 day	1 week	2 months	1 year	5 years
1000	A					
900		A	A	A		
800		A	A	A		
750		A	A	A		
700			A	A	A	
600			A	A	A	
500				SS	SS	SS
400				SS	SS	SS
300				SS	SS	SS

Note: "A" indicates alumina crucible; "SS" indicates stainless steel crucible

Table 3

CRYSTALLINE PHASES GLASS 76-68

	Observed Maximum Concentrations (wt.%)
RuO_2	1.4
Pd	1
$(Zn, Ni)(Fe, Cr)_2O_4$	Trace
$(Ce, Zr, RE^{3+})O_{2-x}$	5
Zn_2SiO_4	14
$(Ca, Sr, Ba)MoO_4$	6
$Ca_2(RE^{3+})_8(SiO_4)_6$	3

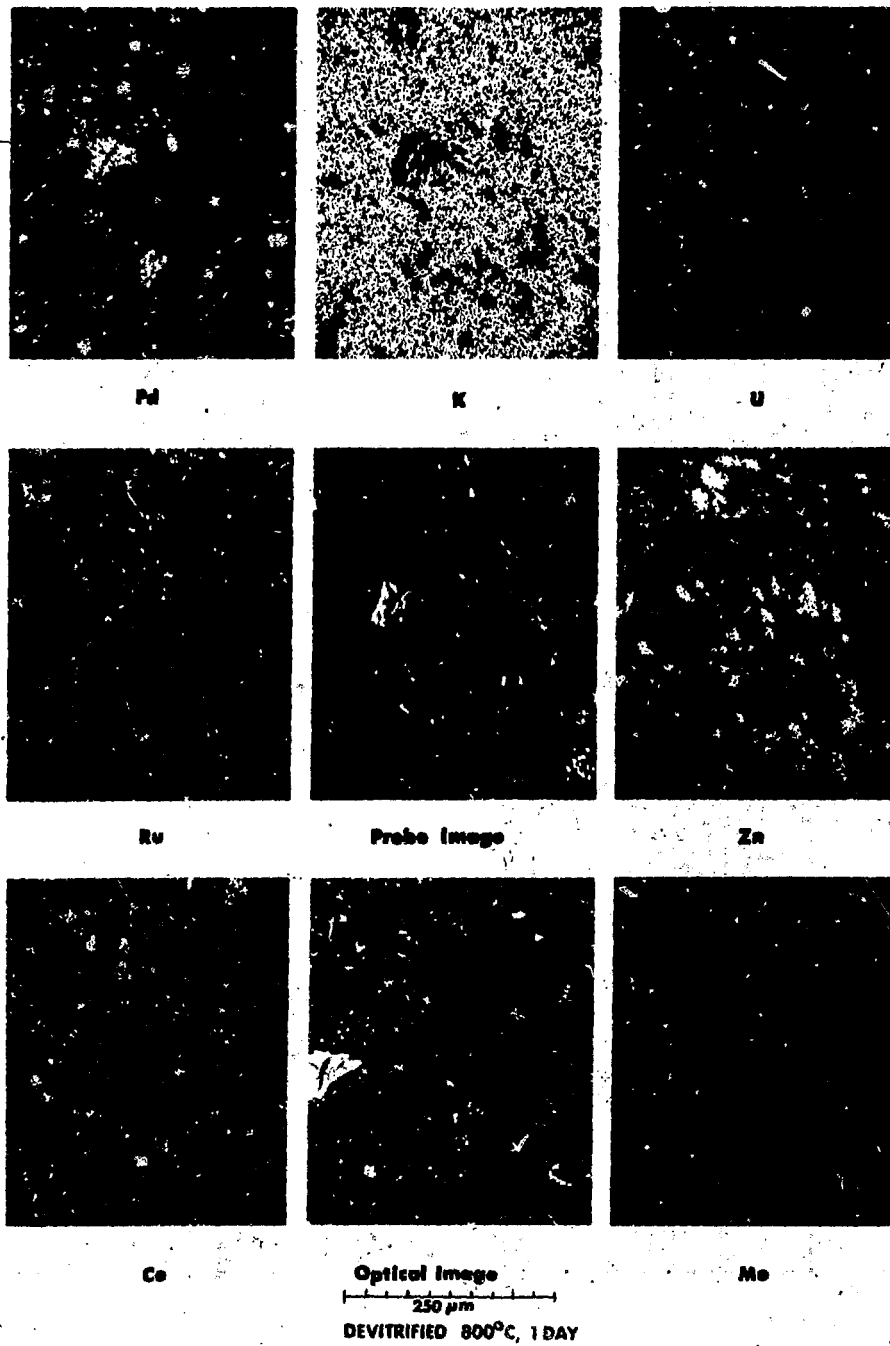


Figure 2. X-ray Fluorescence Maps of Glass (72-68), Devitrified at 800°C.

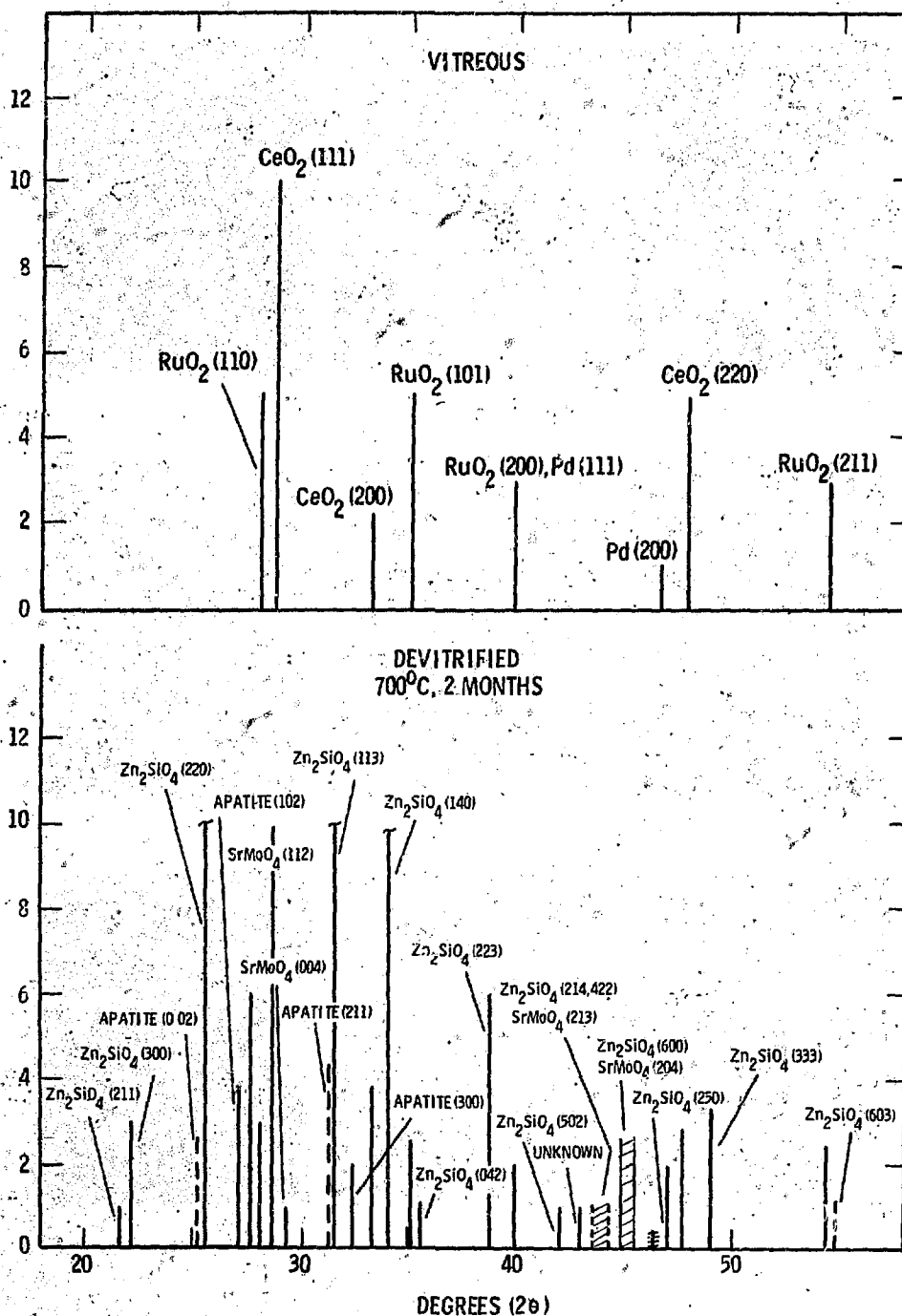


Figure 3. X-ray diffraction traces for as-prepared and devitrified glass (72-68).

From free energy considerations, it is expected that partial crystallization of some phases may occur at temperatures below a liquidus temperature which will vary with each phase involved. It is to be expected that increasing fractional crystallization will occur at lower temperatures until diffusion and/or nucleation kinetics become controlling. Figure 4 shows results for formation of Zn_2SiO_4 , demonstrating a regular approach to the equilibrium concentration for the various isochronal curves. No crystallization occurs at temperatures of 500°C and lower even after one year of annealing. Figure 5 shows fractional ingrowth data estimated from equilibrium concentration versus temperature curves for both the silicate and molybdate phases, plotted as $\ln F$ versus $1/T$. The slope is approximately $\Delta H^\circ/2R$ in both cases, yielding heats of crystallization as indicated, which are of the expected magnitude. The liquidus temperatures ($\ln F = 0$) are 980°C and 890°C for the zinc silicate and molybdate phases, respectively. The kinetics of formation of the Zn_2SiO_4 phase, in particular, have been investigated in much more detail than appropriate for discussion here. As shown in Figure 6, reasonable sigmoidal ingrowth curves can be generated for a given set of conditions, however, the details of sample preparation (for example vitrification temperature, crucible type, sample morphology) have significant influences on data obtained. This means a rather qualitative understanding of kinetics is obtained with respect to behavior in actual full-scale canisters. Direct examination of full-scale preparations will be required to obtain a good correlation to laboratory kinetic data.

Finally, Figure 7 compares x-ray diffraction traces of devitrified glass (72-68), now nearing completion of its characterization, and glass (76-68) which will be one of several glasses studied during the next year. The new glass shows significant promise with respect to devitrification stability, with only small crystals of simple oxides (and Pd) formed which are expected to be radiation damage resistant and low leachable phases.

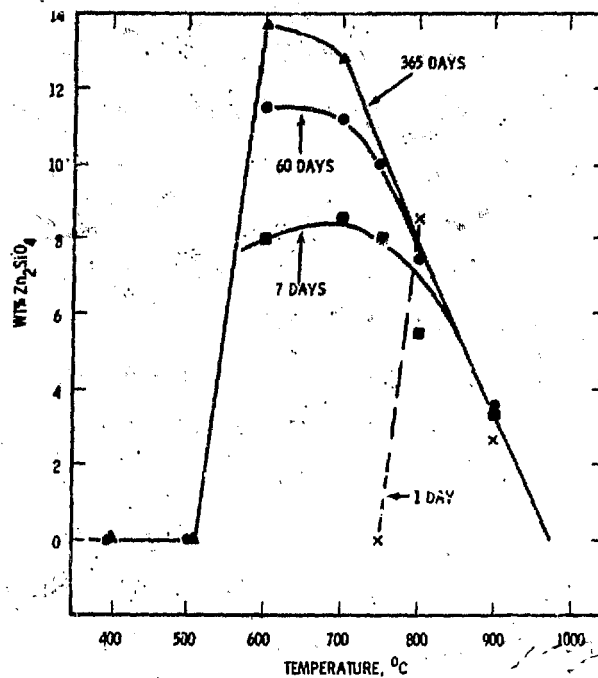


Figure 4. Weight Percent Zn_2SiO_4 Versus Temperature After Times as Indicated.

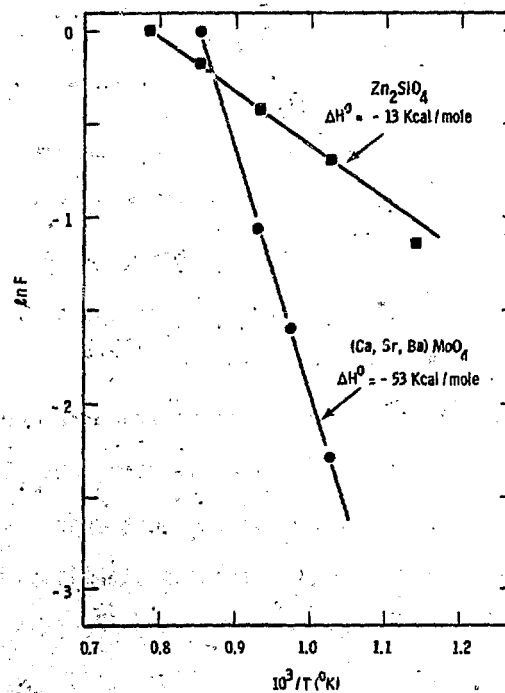


Figure 5. Fractional Crystal Yield Plotted Versus $1/T$ for Zn_2SiO_4 and $SrMoO_4$.

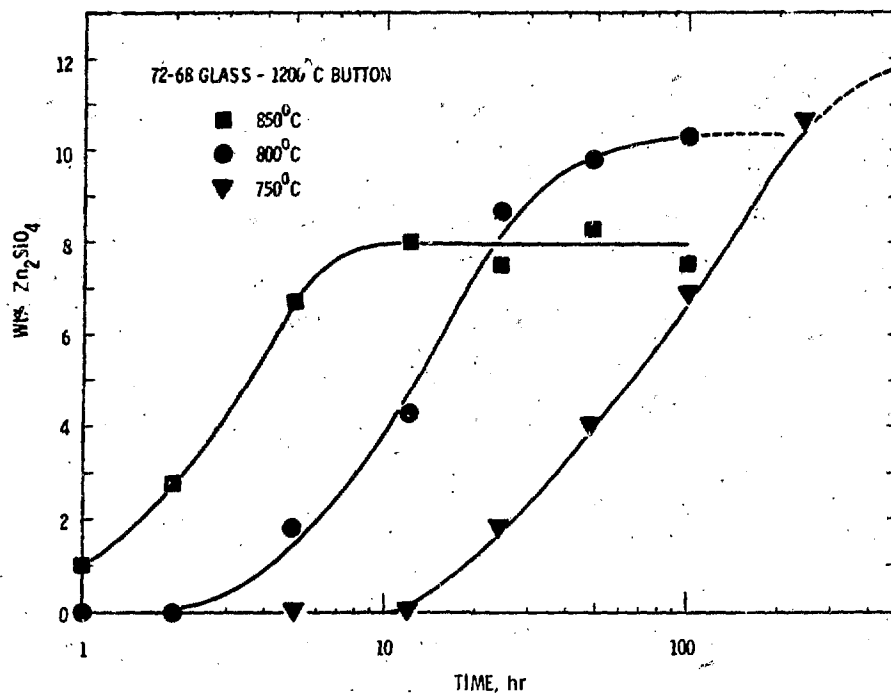


Figure 6. Isothermal Ingrowth Curves for Zn_2SiO_4 , Plotted as wt.% Versus Log t(hours)

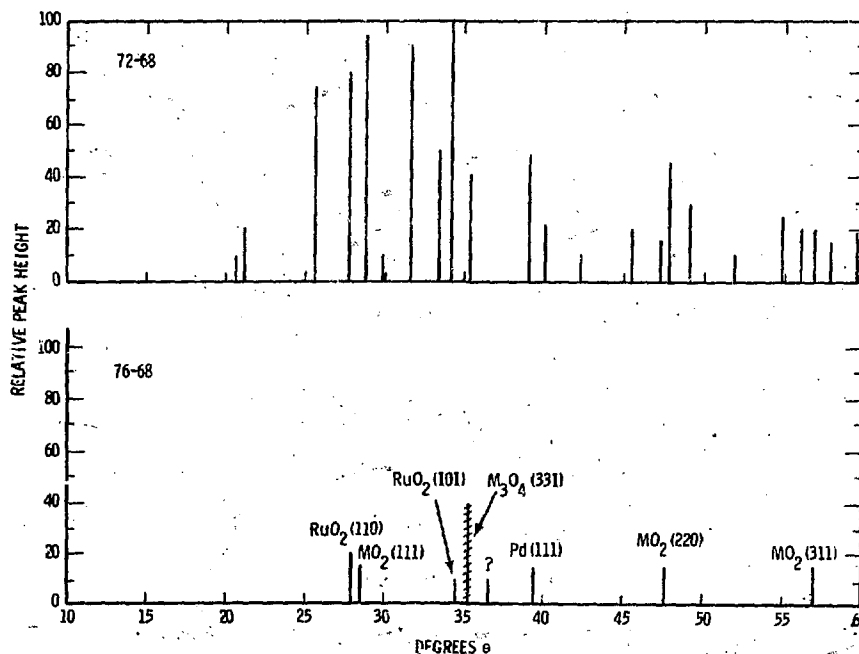


Figure 7. Comparison of X-ray Diffraction Patterns for Devitrified Glasses (72-68 and 76-68).

RADIATION DAMAGE

The radiation damage work undertaken at PNL relies heavily on doping methods using the alpha emitter ^{244}Cm ($t_{1/2}$ - 18 years), which can simulate 100-1000 years of damage per year of experimentation. A program using ion bombardment techniques has been initiated to extend understanding to beyond 10^6 years. In the curium doping work, stored energy, volumetric changes, helium diffusion, and leaching behavior have been investigated. As helium is not expected to be a problem (3) unless actinides concentrate in devitrification phases (also under study), this area will not be further discussed here. Leaching changes, which are small in vitreous samples, will also not be considered.

Table 4 shows some displacement rate calculations from the various radiation damage sources present in radioactive wastes. Note that even at 12 years, alpha decay produces 95% of all displacements, a fraction which greatly increases at long times since the major beta emitters have 30 years half-lives (^{137}Cs , ^{90}Sr). Figure 8 shows cumulative alpha doses as a function of time for UO_2 and mixed oxide fuel wastes. Data for simulated waste glasses at this time extends to the 10^{18} alpha/gram level. To summarize, no major property changes have been observed but continued radiation damage studies are needed, particularly to higher damage levels to more clearly establish the magnitude of potential problems.

Figure 9 shows typical stored energy release curves obtained by differential scanning calorimetry (DSC) for glass 72-68 after sustaining various alpha damage levels as indicated. A regular trend is apparent and a two stage release mechanism is suggested. The important feature is the very broad temperature range over which release occurs, suggesting a variable activation energy for annealing, as has been observed by other investigators studying damage annealing in simple glasses.

Figure 10 shows a plot of stored energy versus alpha dose, for glasses doped at the 1 wt.% and 8 wt.% levels, suggesting that dose rate effects are not too important,

Table 4

ENERGY DISSIPATED IN ELASTIC COLLISIONS BY VARIOUS NUCLEAR RADIATIONS, AND ACCUMULATIONS OF ELASTIC-COLLISION-ENERGIES IN RADIOACTIVE WASTES.

Nuclear Particle	Energy Dissipated in Elastic Collisions, KeV	Cumulative Number of Particles in Wastes, (a) Aged 12 and 80 Years ($10^{17}/\text{cm}^3$)		Cumulative Amount of Collision Energy Dissipation in Wastes, (a) Aged 12 and 80 Years ($10^{19} \text{ KeV}/\text{cm}^3$)	
		12 yr	80 yr	12 yr	80 yr
α -RM (100 KeV)	100(b)	8.1	17.1	8.1	17.1
α (6 MeV)	4 to 8(b,c)	8.1	17.1	0.3 to 0.6	0.7 to 1.4
B(>0.5 MeV; average = 1.5 MeV)	<0.1(d)	3	5	<0.3	<0.5
γ (2 MeV)	<<0.1(e)	<3	<5	<<0.3	<<0.5
Fission recoil	5000(f)	$2 \times 10^{-5}(g)$	$4 \times 10^{-5}(g)$	0.001	0.002

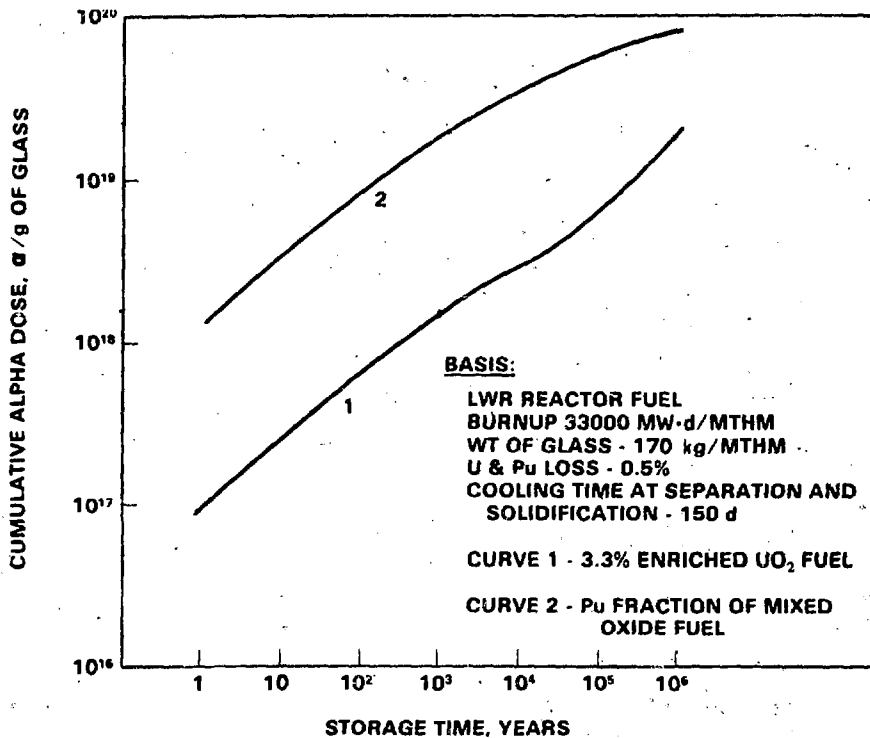


Figure 8. Cumulative Alpha Dose Versus Storage Time.

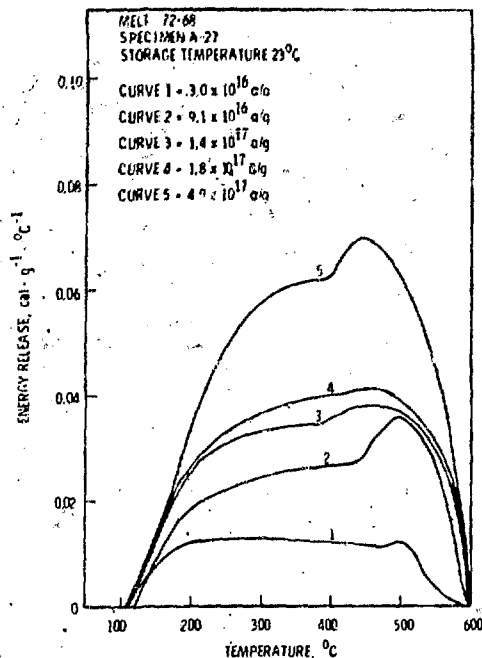


Figure 9. Energy Release in $\text{cal} \cdot \text{g}^{-1} \cdot ^\circ\text{C}^{-1}$ Plotted Versus Temperature After Various Accumulated Alpha Doses, as Indicated.

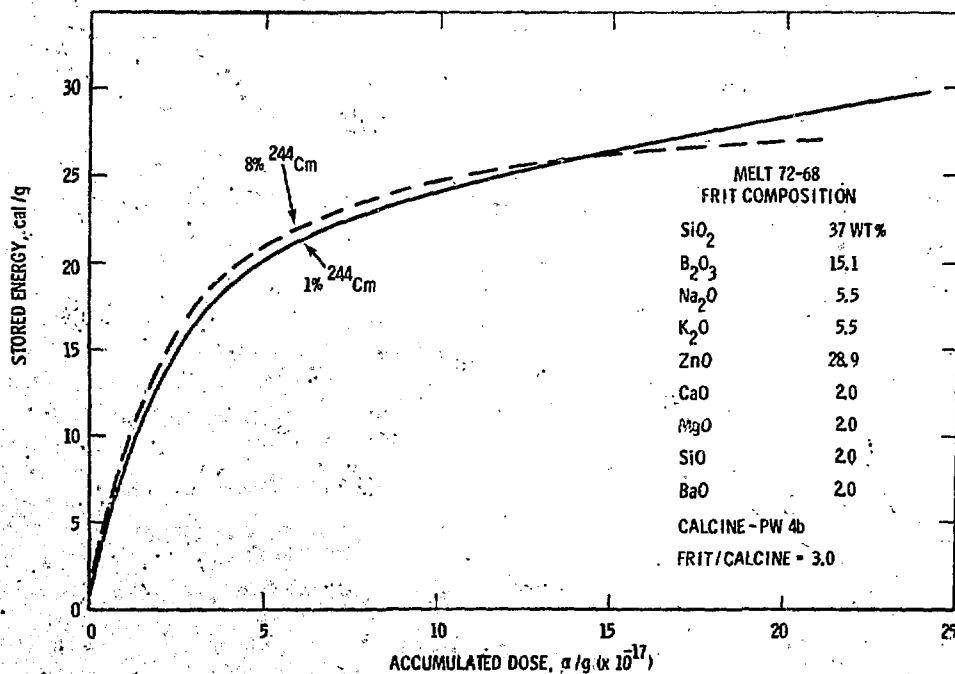


Figure 10. Stored Energy in cal/g Versus Accumulated Dose for Specimens Doped With ^{244}Cm at 1 wt.% and 8 wt.%.

since the curves are in good agreement. Figures 11 and 12 show energy storage ingrowth for two other glasses of much different composition (high lead and high silica). Within experimental error all of these glasses have the same energy storage ingrowth/dose dependence. With respect to safety analyses, projected energy storage levels of ~ 50 cal/g may be expected at 10^6 years. If released adiabatically (which is not likely), a maximum temperature rise of $\sim 200^\circ\text{C}$ might occur--not considered a serious concern.

The density changes which accompany radiation damage are unique to each glass as can be seen in Figure 13. Both positive and negative changes are observed, for reasons not yet clear. A maximum change of 1% was observed for the 8% Cm doped 72-68 glass after 12×10^{17} alpha/gram with reversal to lower density at higher damage levels. Obviously more work needs to be done, but the potential exists to design a glass with minimum volume changes due to radiation damage.

Crystalline phases which might occur in devitrified glasses or in purposely crystallized waste forms are a much greater cause for concern since volume changes which accompany metamictization are known to be large. Figure 14 shows volume changes which occur in several curium containing compounds and for the mineral zircon, alpha-recoil damaged by incorporated thorium and uranium. The bottom curve shows the behavior of radiation damage resistant phases (like PuO_2) which remain crystalline to very high damage levels but undergo $\sim 1\%$ volume changes due to the crystallographic defects introduced. Large volume changes in selected phases of a heterogeneous system must clearly be a subject of concern in devitrified glasses, glass ceramics or fully crystallized waste forms.

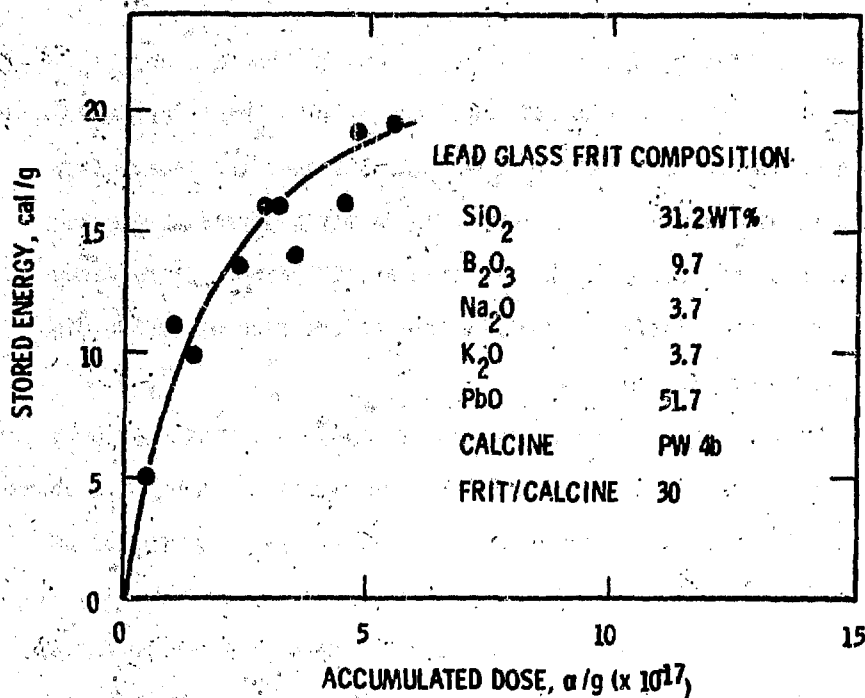


Figure 11. Energy Storage in High Lead Glass Versus Dose.

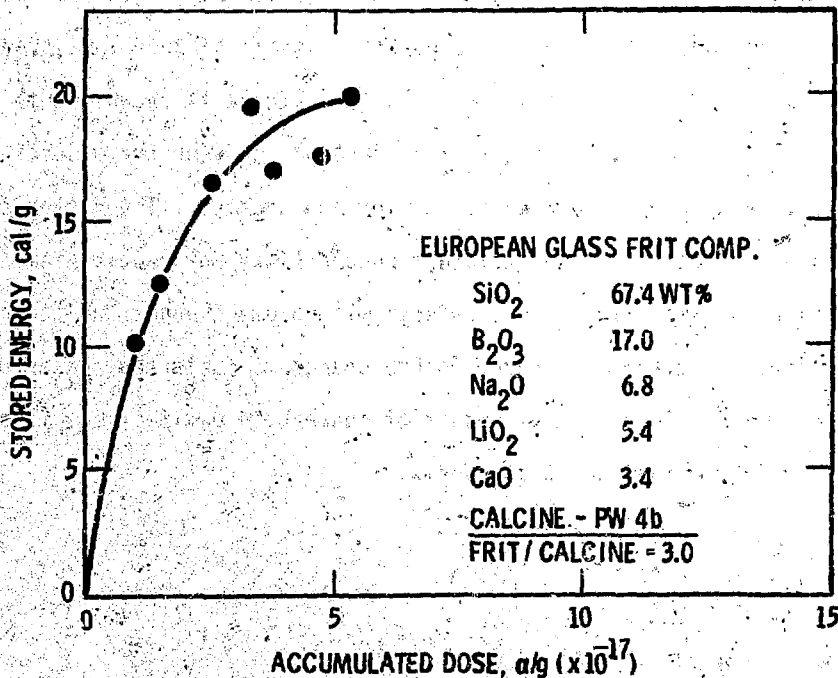


Figure 12. Energy Storage in High Silica Glass Versus Dose.

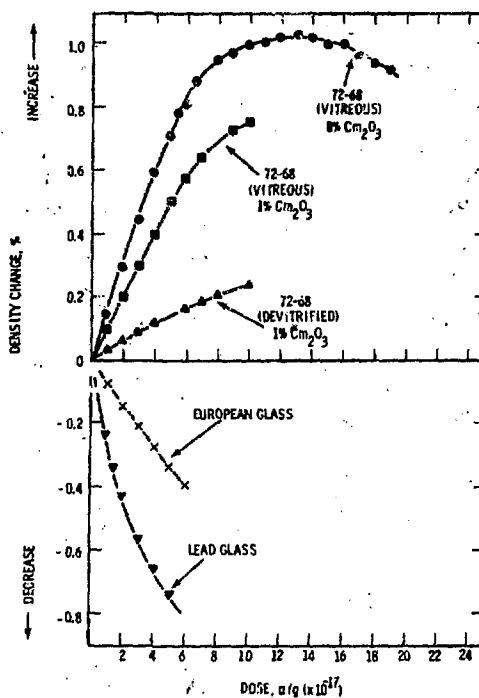


Figure 13. Density Changes in Various Glasses, as a Function of Dose.

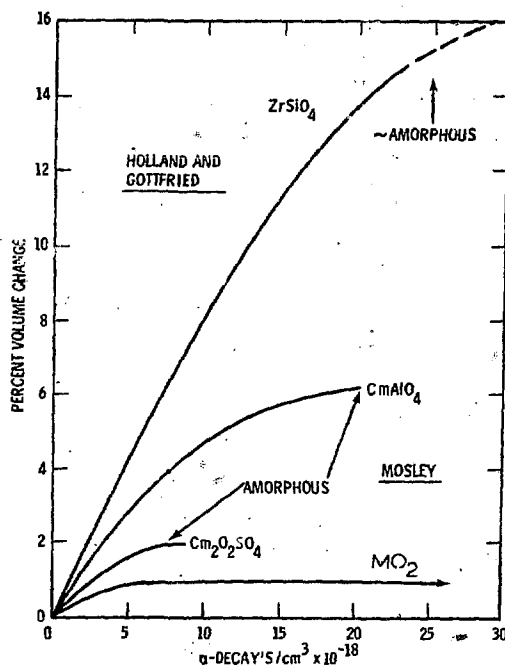


Figure 14. Alpha-recoil Induced Volume Changes in Some Crystalline Compounds, as a Function of Dose.

SUMMARY

The results presented in the preceeding discussion demonstrate that detailed and reproducible data can be obtained for complex waste glasses. For the major glass composition examined, thermal treatment was shown to cause formation of several crystalline phases which contribute to an increased leachability. Although not discussed in detail here, Zn_2SiO_4 formation results in microcracking due to a thermal expansion mismatch with the glass matrix and SrMoO_4 has a higher leachability than the glass matrix. The temperature dependence describing equilibrium concentrations of these two phases and a qualitative understanding of ingrowth kinetics have been established--hence conditions necessary to eliminate their formation during processing and early storage, are known.

Radiation damage effects, when extrapolated to long times, suggest energy storage of ~ 50 cal/gram and either positive or negative density changes occur (depending on the glass composition) in the 1% range. No radiation damage-related changes of serious concern have been found for homogeneous glasses by ^{244}Cm doping experiments now approaching a simulated damage time of $\sim 10^3$ years (for UO_2 fuel wastes). More work is needed concerning heterogeneous damage which will occur in devitrified glasses.

As a final point, the complications with respect to understanding behavior of polyphase systems with respect to either radiation damage or leaching behavior, are self evident. Homogeneous glasses with improved leach resistance, and thermal and radiation stability are clear objectives for future glass development.

ACKNOWLEDGMENT

Contributions to this study by J. Wald, J. Westsik, J. Gose, and R. Stephens are gratefully acknowledged.

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CERAMICS AND GLASS CERAMICS AS HIGH LEVEL WASTE FORMS

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INTRODUCTION

Each of the nuclear nations of the world is currently emphasizing borosilicate or phosphate glass as the commercial nuclear fuel reprocessing high level waste (HLW) form. In the U.S. and West Germany, ceramics and glass-ceramics, respectively, are also under consideration as "advanced" or "alternative" HLW forms. Glass, of course, is also a "ceramic" material, but for the purposes of this workshop we define for ceramics and glass-ceramics the following characteristics vis-a-vis glass.

- Products are designed to be predominantly or totally crystalline.
- Depending on the product, the HLW form is either in or nearer to its stable thermodynamic equilibrium state when formed.
- In several of the products, waste loading is high by a factor of two to three, with little or no sacrifice in leaching resistance.
- Most of the products remain solid to higher temperatures and have lower HLW volatility.
- More information is available on the structural environment of each HLW nuclide.

HLW glass will also be partially crystalline because it contains undissolved oxides (e.g., CeO_2 , ZrO_2 and RuO_2) and metals (e.g., Pd, Rh, and some of the Si metal added to control oxidation state) plus devitrification products (e.g. Zn_2SiO_4 in zinc borosilicate formulations). However, the intention is not to further crystallize these glasses.

The most important potential advantage of crystalline waste forms is the elimination of the thermodynamic driving force for phase transformations in the stored waste.

These transformation can be: further devitrification in glass, crystalline phase transitions, or interaction of two or more crystalline phases during storage to produce new unexpected phases. These devitrification products and new phases can, and in some well documented cases do, have less desirable properties than the originally prepared HLW glass.

The advantage of higher waste loading for crystalline materials can be important if reduction in the number of waste canisters is desired. Of course, higher waste loading means more heat per standard canister, but some of the ceramics can be stored at higher temperatures than are now projected for HLW glass.

Finally, when a waste form is crystalline, one can use routine x-ray and electron diffraction combined with scanning electron microscopy (SEM) to pinpoint the crystal chemical environment of any nuclide. Judgments can then be made on whether to leave the nuclide in that crystalline phase or to modify the composition and processing to produce a new, more desirable phase. If little data is available on that phase, it can be synthesized and evaluations of the relevant properties (leachability, thermal stability, susceptibility to radiation damage, etc.) can be made. The familiar term, "tailor-making," has been adopted to describe this process and several examples of this atomic scale tailor-making in ceramic waste forms will be pointed out below. Similar characterization of glasses is far more difficult making them less amenable to tailoring.

HLW liquid is a nitrate solution (or for some ions, an oxide suspension or sludge) of the components listed below in Table 1.

Simple HLW calcine is a mixture of the oxides of these components prepared by rapid drying and heating in the range 500-800°C in spray or fluidized bed calciners. The product is generally an x-ray amorphous powder. If calcine is fired at temperature above ~900°C, some crystallization will occur, so that fired calcine could be included here as a ceramic product. Some of the early Penn State work was concerned with identifying the phases crystallized in fired PW-4b calcine, (1). Some of which are listed in Table 2.

Table 1

TYPICAL HLW COMPOSITIONS*

Component	Mole Percent		
	PW-4b	PW-7	PW-7a
Rare Earths (RE)	26.4	30.9	20.5
Zr	13.2	9.2	6.1
Mo	12.2	8.2	5.5
Ru	7.6	5.1	3.4
Cs	7.0	4.7	3.1
Fe	6.4	8.7	5.8
Pd	4.1	2.8	1.8
Sr	3.5	2.3	1.6
Ba	3.5	2.3	1.6
[PO ₄]	3.2	8.7	5.8
U	1.4	9.6	6.3
Rb	1.3	0.9	0.6
Na	--	0.9	34.0
Am+Cm+Pu	0.2	0.2	0.2
Others	9.8	5.5	3.7

* PW is ERDA shorthand for Purex process Wastes. PW-4b and PW-7 are "clean" HLWs in the sense of low Na content from processing PW-7a is a "dirty" HLW due to the high Na content PW-7 contains an excess of gadolinium used as a burnable poison plus more iron, [PO₄], and uranium and some sodium. PW-7a is typical of HLW to be generated by Allied General Nuclear Services, Barnwell, South Carolina.

Table 2

PHASES IN FIRED PW-4B

<u>Solid Solution Phase</u>	<u>Crystal Structure</u>
(Sr,Ba)MoO ₄	Scheelite
(Ce,RE,Zr,U)O _{2±x}	Fluorite
RE(Fe,Cr)O ₃	Perovskite
Ni(Fe,Cr) ₂ O ₄	Spinel

In other words, the refractory oxides react and crystallize into familiar phases according to their molar ratios, while the volatile species (Cs, Rb, Ru, Te, some Mo, as oxides or metals) simply vaporize. The calcine powder is not considered to be a good final product because of its poor thermal stability and its high leachability and mechanical dispersibility, (2).

There are seven ceramic/glass-ceramic HLW forms on which significant R&D have been performed.

<u>Product</u>	<u>Site</u>	<u>References</u>
Fusion-cast	PNL (WSEP)	3
Ceramic sponge	LASL	4
Ceramic matrix-hot press	Penn State	5,6
Sintered calcine-glass	PNL and INEL	7, 8
Glass-ceramic	HMI (Berlin)	9
Titanate ceramic	Sandia-Alb.	10
Supercalcine	Penn State	11,12

The first product was one of the HLW solids evaluated in the Waste Solidification Engineering Prototypes (WSEP) program. A crystalline ceramic was prepared by casting a melt consisting of "ortho- and pyrophosphates" into a storage canister. The product crystallized on cooling below 800°C. It proved to be unsatisfactory because its water leachability was 10 to 10³ times that of HLW borosilicate glasses. However, it was the least dispersible HLW solid evaluated in the WSEP program.

In the ceramic sponge process, HLW liquid is absorbed into porous bisque-fired clay bodies followed by drying and firing at 1200-1400°C to partially vitrify the bodies and fix the HLW species. The products had very low Cs but high Ru vaporization losses on firing and had low Cs and Sr leachabilities. This work was performed in the early 1960's and has not been investigated further.

SINTERED CALCINE

The next three products share a common concept with the ceramic sponge and with each other, namely, that of protecting the HLW calcine by encasing it in, or reacting it with, a glass or ceramic matrix. Partial vitrification of the product is used in each to promote sintering and densification. In the hot pressed ceramic matrix product, ~30 wt% of HLW calcine is mixed with powdered quartz and a small amount of a low leachability glass frit and hot pressed at 1100-1200°C and 2000-4000 psi. The product has comparable leachability, but greater thermal stability, than glass with the same level of waste loading. Laboratory scale demonstration was completed in 1975 using

description is (2):

Liquid HLW is calcined and melted with the addition of glass frit. The melt is cast in small blocks or plates sized so that temperature gradients will be small. The blocks are cooled rapidly so that they remain completely vitreous and are then taken through a carefully programmed thermal treatment to promote controlled nucleation and crystallization. The blocks are stacked in a canister and the annulus filled with metal for enhanced heat transfer.

Reference 2 suggests that "a glass-ceramic is stronger than glass, would not be as susceptible to uncontrolled devitrification at high storage temperatures and would have leach resistance similar to glass."

Results of the HMI cold lab-scale HLW glass-ceramics investigations were published recently (9) and a few highlights are:

- Process temperatures are: melting, 1100-1400°C; nucleation, 530-700°C; crystallization, 630-960°C.
- Waste composition similar to PW-7a; glass of the alkali or alkaline earth aluminosilicate types.
- Bulk leachabilities are slightly greater in the crystallized product than in the parent glass.
- Nuclides of concern (e.g. ^{90}Sr , ^{137}Cs) are crystallized in tailor-made host phases.

This product is the first of the three to be described here which are "tailor-made" on the atomic scale or which utilize "molecular engineering." Consider as an illustration the troublesome and hazardous nuclide ^{137}Cs . The HMI group makes it clear that one of their first goals in tailor-making a HLW glass-ceramic was to fix Cs in pollucite, $\text{CsAlSi}_2\text{O}_6$. For this reason they always use aluminosilicate-based formulations. In their paper, they demonstrate pollucite crystallization (and coincident Cs depletion in the residual glass) through SEM photomicrographs of $\text{CsAlSi}_2\text{O}_6$ crystals. The mineral is the most common host for Cs (and Rb, another HLW ions) in nature. Because it crystallizes from igneous formulations just as complicated chemically as HLW, nature has provided some indication of its stability. Pollucite is highly resistant to water leaching of the Cs (16) and has good thermal stability (17). (An extensive study of the crystal chemistry, phase relations,

a non-radioactive but otherwise full-composition clean waste (PW-4b). Further work has not been scheduled because of the difficulties with remote hot pressing under high radiation conditions. As the name implies, the sintered calcine-glass products are a mixture of 50-70 wt% HLW calcine and either a suitable glass frit or a mixture of glass-making raw materials. The process description is, (2):

Calcine is mixed with a flux and a binder-lubricant, which can be water. If large disks are desired, the mixture is pressed to a low-profile, thin-walled steel container. If smaller pellets are to be formed, the powder is fed to a pelletizer. The shaped mixtures are then sintered with the large disks requiring a low pressure pressing while still hot to conform the product to the container. After cooling, the disks could be loaded directly into the canister. The pellets would require a matrix and could be coated.

The INEL version of this process is illustrated in Figure 1 supplied by J. R. Berreth of INEL.

Some data on the properties of the sintered calcine-glass products prepared in the laboratory are available. Some of the crystalline phases resulting from the reactions between the calcine and glass have been reported and are given below:

PW-4b + zinc borosilicate
glass (PNL) (13,14)

(Ce,RE,Zr)O_{2-x}

(Sr,Ba,Ca)MoO₄

(Ni,Zn,Mg,Co) (Fe,Cr)₂O₄

REBSiO₅

~PW-7 + Ba-Zn-Ti-
aluminosilicate (INEL) (15)

RE₂Zr₂O₇

Fe₃O₄

CeO₂

Gd₂O₃

GdFeO₃(?)

The INEL phases should be considered as structure types of complex solid solution phases rather than the simple compounds reported. The products are relatively dense and hard and have leachabilities up to several times that of laboratory borosilicate glass.

GLASS-CERAMICS

The "classical" nucleation and growth glass-ceramic approach to a HLW form has not been utilized to any extent in the U.S. It is under active investigation in West Germany, principally at the Hahn-Meitner Institute (HMI) in Berlin. The process

leachability and thermal stability of pollucite is presently in progress at Penn State.) Pollucite is the Cs fixation phase in the three tailor-made waste forms, glass-ceramic, titanate ceramic and supercalcine.

One problem with the glass-ceramic approach is that in order to make the original glasses fusible at reasonable temperatures, additions of fluxes such as B_2O_3 must be added to the aluminosilicate formulations. This leaves a relatively leachable borate-rich residual glass after crystallization that makes the bulk leachability slightly higher than the parent glass. Leachabilities of the ions (Cs, Sr, etc.) fixed in the crystalline phases have not been reported, but these should be significantly lower than the parent glass.

The HMI glass-ceramic process has been demonstrated both cold and with radioactive waste on a lab scale and is currently in the radioactive pilot scale stage of testing, (18).

TITANATE CERAMICS

The titanate ceramic HLW form is the hot pressing consolidation product in the Sandia Solidification Process. Reference 2 gives the process and description as follows and as shown in Figure 2:

HLW is neutralized to pH = 1 with NaOH and clarified by centrifugation. The clarified waste is then almost completely decontaminated ($<10^{-5}$ Ci/ml total activity, mostly ruthenium, cesium, and technetium, and $<10^{-10}$ Ci/ml α -emitters demonstrated on a laboratory scale) by ion exchange with sodium titanate (ST). Cesium is subsequently removed by ion exchange with a zeolite, and the remaining trace wastes such as ruthenium and pertechnetate ions are removed with an anion exchange material and other reagents. The exchanged ST and zeolite are removed as slurries and combined in slurry form with the suspended solids which were removed in the clarification step. This mixture of slurries is dewatered and dried on a pan filter, then consolidated by pressure sintering, the only high-temperature step in the process.

The process and its product characterization are described more completely later in this report.

The hot pressed titanate ceramic products are largely crystalline. Only a small amount of alumina-silica from the zeolite and silica from the oxidation of the Si metal additive is non-crystalline. About half of the product is rutile, TiO_2 . Silicon metal is added to maintain a reducing environment, so many waste constituents

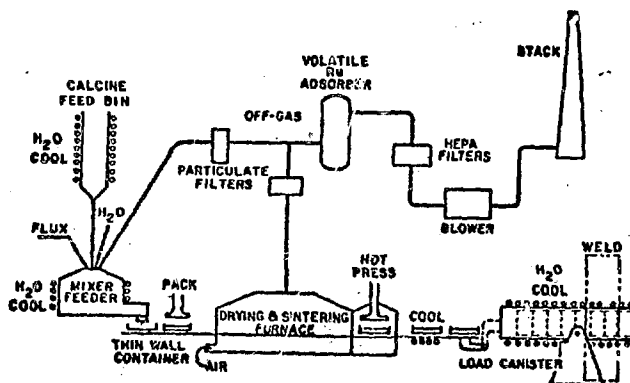


Figure 1. INEL Waste Sintering Process

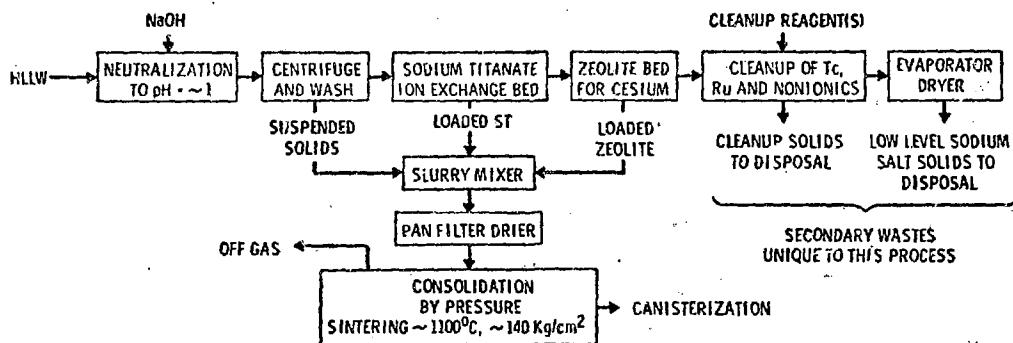


Figure 2. Titanate Ceramic Process

occur as metals (Mo, Pd, Rh and perhaps Te and Fe). Alkaline earths and rare earths form stable and refractory titanates. In the early stages of the work it was found that alkali (Cs, Rb, Na) titanates were formed during consolidation, but these had poor leaching resistance and thermal stability. The zeolite exchange step was added and this resulted in the fixation of Cs and Rb in pollucite. Other oxides occur uncombined with titania (CeO_2 , UO_{2+x} , ZrO_2). The presence of each of these phases was identified or confirmed using selected area electron diffraction combined with scanning transmission electron microscopy (STEM).

Based on what has been learned to date, it is likely that the titanate ceramic is close to thermodynamic equilibrium under HLW storage conditions in a closed system (such as a sealed canister). The individual phases, TiO_2 , titanates, aluminosilicates, oxides and metals, are apparently compatible but this has yet to be confirmed by long term firings at waste storage temperatures. The stability at elevated temperatures in air may be different than in a closed system because some of the metals reoxidize.

The Sandia Solidification Process, as applied to commercial HLW, has been demonstrated both cold and "hot" (radioactive) on a lab scale is currently being tested with ERDA Defense Wastes at Hanford.

SUPERCALCINE

The last HLW ceramic product to be discussed is unique because it has been based on "molecular engineering" since its conception. The basic premise of this tailor-made ceramic HLW solid is that modifications can be made to the HLW liquid composition through the addition of selected liquid additives, so that when the liquid is calcined and given additional heat treatment, an assemblage of refractory, leach-resistant and thermodynamically compatible crystalline phases is produced. Because this product shares a common processing step with HLW calcine, it has been called for shorthand purposes, "supercalcine." The iterative procedures used to select the fixation phases for the troublesome and hazardous HLW nuclides and to confirm compatibility with other crystalline phases is described in a recent article (12).

The tailor-making of an assemblage of crystalline phases by modifying the crystallization behavior of HLW ions with additives is illustrated by the simplified supercalcine formulation in Table 3. Table 4 shows demonstrated or projected crystal chemical roles of all HLW ions. The nine crystalline phases in the phase formation model have all been identified in the supercalcine products prepared from formulations using the cold engineering-scale equipment at PNL. The four additives to the simulated HLW liquid were nitrate solutions of Ca, Sr and Al plus stabilized silica sol (duPont LUDOX-AS). This is one example of a successful supercalcine formulation. Other formulations for dirty HLW and new phase formation models are currently under development.

As prepared in the spray calciner, supercalcine is a very fine, x-ray amorphous, powder. It will crystallize into the designated phases when heated above 1000°C for a short duration (10 min +). There are three potential application of supercalcine.

- . Improved calcine in canister
- . Monoliths of pure Supercalcine in canister
- . Core of the Multibarrier Waste Form

As stated in Reference 2, "if an unconsolidated calcine continues to be an acceptable waste form, supercalcine ... concepts can be introduced into the flow sheets immediately which will improve the stability and insolubility of some of the radioactive waste constituents." As a second option, supercalcine can be cold pressed and fired or hot pressed into shapes which can be simply stacked in the canister. Firing pressed pellets of supercalcine at ~1100°C yields a 90-95% dense product with Soxhlet (boiling distilled water) leachabilities approximating those of HLW glass. Hot pressing of supercalcines at ~1100°C has been demonstrated on a laboratory scale and results in improved product characteristics.

The third option for utilization of supercalcine, is as a core of a multibarrier waste form as shown in Figure 3. PNL and Penn State are both working on the supercalcine multibarrier concept. Spray Supercalcine is formed into 1-5 mm diameter cores

Table 3
TYPICAL SUPERCALCINE FORMULATION

mMoles in HLW*	Phase Formation Model	Required Additives
340 RE ³⁺	30 Ca ₂ RE ₈ [SiO ₄] ₆ O ₂ [A _{ss}]	60 Ca 120 Si
100[PO ₄]	100 REPO ₄ [M _{ss}]	-
100 U 100 Zr 50 Ce	250 [(U,Ce,Zr)O ₂ [F _{ss}]+ (Zr,Ce,U)O ₂ [T _{ss}]]	- - -
100 Mo	100SrMoO ₄ [S _{ss}]	100 Sr
100 Fe 10 Cr 5 Ni	115 [(Fe ₂ O ₃) _{ss} +Ni(Fe,Cr) ₂ O ₄ [SP _{ss}]]	-
60 Ru	RuO ₂	-
25 Ba 25 Sr	in S _{ss}	-50 Sr
55 Cs 10 Rb 10 Na	75(Cs,Rb,Na)AlSi ₂ O ₆ [P]	75 Al 150 Si
1090 mM of HLW ions require these additives to form supercalcine		60 Ca 270 Si 50 Sr 75 Al

* Concentrations approximate ERDA's PW-7

Table 4
CRYSTAL CHEMICAL ROLES OF HLW
IONS IN SUPERCALCINE
("Clean" HLW)

Waste Ion*	Crystalline Phase
RE^{3+} (La, Ce**, Pr, Nd, Pm, Sm, Eu, Gd, Tb, Dy, Y), $[PO_4]$	$Ca_2RE_8[SiO_4]_6O_2$ $[A_{ss}]$ and/or $REPO_4$ $[M_{ss}]$
U, Zr, Ce**	$\left\{ \begin{array}{l} (U, Ce, Zr)O_2 \text{ } [F_{ss}] \\ \text{and} \\ (Zr, Ce, U)O_2 \text{ } [T_{ss}] \end{array} \right.$
Mo, Sr, Ba	$(Sr, Ba, Ca)MoO_4$ $[S_{ss}]$
Cs, Rb, Na	$(Cs, Rb, Na)AlSi_2O_6$ $[P]$
Ru	RuO_2
Fe, Cr, Ni	$\left\{ \begin{array}{l} (Fe_2O_3)_{ss} \\ \text{and} \\ Ni(Fe, Cr)_2O_4 \text{ } [SP_{ss}] \end{array} \right.$

(tentative)

Pd, Rh	as metals
Tc	in S_{ss} or SP_{ss}
Np, Pu	in F_{ss}
Am, Cm	in A_{ss} and/or M_{ss}
Cd	in A_{ss}
Ag	in P or A_{ss}

* Te is the only PW-7 species for which a role has yet to be demonstrated or projected.

** Ce can crystallize in $F_{ss} + T_{ss}$ under oxidizing conditions and in A_{ss} or M_{ss} under reducing conditions.

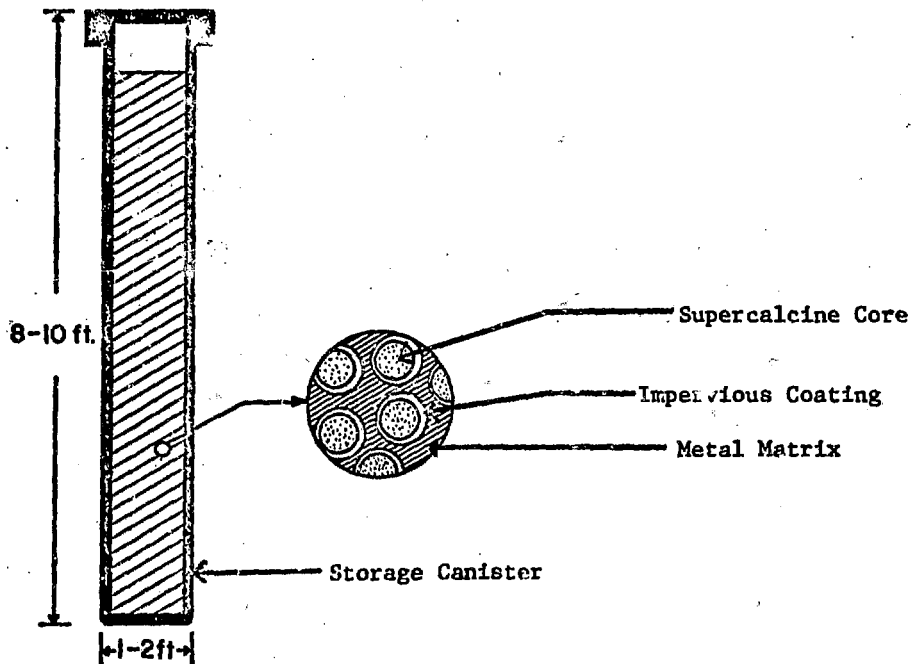


Figure 3. Typical Multibarrier Waste Form Concept

in a disc pelletizer, followed by a crystallization-consolidation firing at $\sim 1100^{\circ}\text{C}$,

(20). Currently, the pellets are given a dual coating of pyrolytic carbon (for leaching protection) and Al_2O_3 (for oxidation resistance) by a CVD process, (21).

The coated cores are encased in a metal matrix to provide a monolithic form plus increased thermal conductivity and impact resistance, (22). Several Soxhlet tests on the coated pellets have shown essentially zero leachability. The critical property of supercalcine relevant to the multibarrier waste form processing is its high thermal stability at the CVD temperatures ($1000\text{--}1200^{\circ}\text{C}$) which yield the highest quality coatings, (23).

Some of the current goals of the multibarrier waste form project are to prepare kilogram quantities of coated supercalcine cores, to demonstrate each of the processing steps in an automated, engineering-scale mode, to determine a cost differential compared to the "reference process" (spray calcination/in-can vitrification) and to estimate the increase in safety in transportation and storage compared to the

reference HLW product (glass).

REVIEW AND RECOMMENDATIONS

Those ceramic and glass-ceramic processes and products on which significant R&D have been performed were discussed. The emphasis in the product descriptions was on the physico-chemical properties likely to affect long term stability, rather than on the bulk engineering properties such as impact resistance. The first recommendation is, for each ceramic waste form under active consideration for HLW solidification and storage, to identify the crystal structural environment of each nuclide of concern (^{90}Sr , ^{137}Cs , ^{99}Tc , ^{106}Ru , ^{239}Pu , etc), duplicate this environment in a pure phase synthesis and determine the relevant properties (leachability, thermal stability, susceptibility to radiation damage and transmutation effects and their effect on properties, etc.). As noted above, judgments can then be made on whether to leave that nuclide in a particular phase or whether to tailor-make it into another more desirable phase.

The second recommendation concerns leachability, the most important single property affecting dispersibility of HLW. The term "leachability" has been used in this report as if it were a well-established concept, measured by universally accepted techniques. The real situation is just the opposite. Measurements by the same technique, in the same laboratory, on the same material often give results differing by factors of 2 to 10. Between laboratories and by different techniques, the situation is even worse. Leachability, as it pertains to HLW storage, should be measured by standardized techniques (known to yield reproducible results) on standardized or normalized (in surface area) specimens and reported in standard units. There exists the IAEA test and reporting units but they have been criticized and are not universally used. The question of what is a desirable or acceptable leachability value is not a simple one. In addition, all waste forms may show some change in leaching resistance with storage time due to thermal and radiation-transmutation effects. It will involve also the compatibility of the HLW form and the geologic storage medium under the P-T-X

conditions of storage. A definitive statement on a required leachability may simply not be possible. However, reproducible benchmark leachability numbers should be prepared, by one or more of the existing techniques, for well characterized minerals, on which the geologic history is known, and for man-made materials which have withstood decades or centuries of weathering or burial.

The third recommendation, calls for a study of the nature and effects of radiation damage and transmutation of the required properties of stored HLW forms.

The fourth recommendation concerns the fundamental scientific information needed for optimal nuclear waste management. Determine for each of the nuclides of concern which are the best host structures (whether crystalline or non-crystalline) from the standpoint of all of the relevant properties for stored HLW. The results may be too expensive or complicated to apply, but they will establish what science and technology are capable of doing with HLW and provide a goal toward which future HLW R&D can strive.

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THE SANDIA SOLIDIFICATION PROCESS A BRIEF OVERVIEW

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INTRODUCTION

A new family of inorganic ion exchange compounds has been developed for the solidification of a wide variety of nuclear wastes. Some attractive features of processes employing these exchangers are the high affinities for all polyvalent cations present in the wastes, the high capacity of the material, its insensitivity to high radiation environments, and the relative ease with which the reacted material can be converted to dense, nonvolatile, leach-resistant ceramics. These ion exchangers also possess attractive properties for the partitioning of nuclides. The major effort in the past has been research and development associated with the use of these materials in the solidification of high level waste from the reprocessing of spent commercial reactor fuel. Current efforts are being directed toward several applications of this approach. In particular, we are studying the removal of ^{90}Sr and actinides from defense wastes in a joint program with Atlantic Richfield Hanford Co., the partitioning of actinides with Oak Ridge National Laboratory, and the selective separation of Cs and other useful nuclides with the Division of Biomedical and Environmental Research. In addition to these specific programs, studies are also underway to characterize the resulting waste forms in terms of both macroscopic thermophysical properties and the microscopic crystalline structure and composition. The latter studies will be extended in the near future to include investigations of actual high level waste stabilized by these inorganic ion exchangers in hot cell experiments. These studies will be conducted using transmission electron microscopy, electron diffraction, and scanning electron

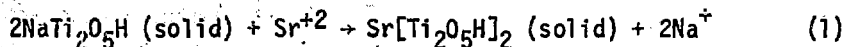
microscopy utilizing apparatus designed for specimens of high specific activity.

ION EXCHANGE CHEMISTRY

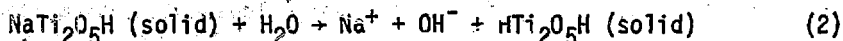
These ion exchange materials have the general formula $M[M'_xO_yH_z]$, where M is an exchangeable cation of the charge $+m$ and M' may be Ti, Nb, Zr, or Ta. Because of economic considerations, a sodium form of the "titanate," $NaTi_2O_5H$ (ST), has received most attention, but $NaNb_2O_6H$ (SN) and $NaZr_2O_5H$ (SZ) have also been studied extensively. Theoretical capacities for the materials are 5.0 meq/g, 3.3 meq/g, and 3.5 meq/g, respectively. The materials contain 10-20 wt% water after drying and actual capacities are reduced accordingly. These capacities have been realized for a broad spectrum of fission product cations in tests with both simulant and actual radwaste solutions.

The exchangers are prepared by reaction of a metal alkoxide with a base in non-aqueous solution followed by hydrolysis. The materials are prepared by reacting the metal alkoxide, $Ti(OC_3H_7)_4$, $Zr(OC_3H_7)_4$, or $Nb(OC_2H_5)_5$, with an alcohol solution of the base containing the desired exchangeable cation. These materials consist of agglomerates of 50-100Å particles with the degree of aggregation of the particles determining bulk density and surface area. Materials with the highest surface areas are most reactive and have been studied most extensively for solidification of aqueous wastes. Attempts to determine the structure or the complex anion in the exchange materials are also underway.

The principal reaction with aqueous waste solutions is simple cation exchange as illustrated for Sr^{+2} ion in Eq. 1.



In general, the affinity of cations for exchange by this reaction increases with valence. The exchangers also react to varying extents with water as illustrated by Eq. 2.



This reaction is significant for ST ($K_{eq} \sim 10^{-6} \text{ moles}^2/\ell^2$) and SZ, but is insignificant for SN and some other "titanate" forms such as $Mg[Ti_2O_5H]_2$. The distribution co-

efficient for standard ST is ~ 200 . For purposes of comparison, SN combines a high affinity for Cs^+ ($K_d > 1000$) with a high overall capacity, while SZ has a very low affinity for Cs^+ ($K_d < 10$). Like ST, both have very high affinities for polyvalent cations.

WASTE DECONTAMINATION

The effectiveness of ST, SZ, and SN materials for solidifying high level waste has been investigated extensively using nonradioactive and tracer level waste solutions simulating the composition expected at the Allied-General Nuclear Services, Barnwell, SC, plant. After materials and contacting methods had been thoroughly tested, demonstrations were conducted at Oak Ridge National Laboratory using high level waste generated by reprocessing small batches of typical spent light-water reactor fuel. This solution was neutralized to $\text{pH} \sim 1$ before use to simulate expected processing conditions. Decontamination factors for key radionuclides are presented as a table in Figure 1. In these experiments, 15-30 ml of feed were passed through each column followed by ~ 30 ml of deionized wash water. Data are reported for the total effluent. In all cases, the cation bed was followed by a Dowex 1-X8 anion exchange bed to remove TcO_4^- and other anionic species to enable accurate determination of the cation decontamination factors. If these results are put in terms of the specific activity of the primary residual solid associated with this process, it is found that the fission product activity is ~ 200 nCi/ml, and the transuranic activity is $\sim$ pCi/ml, well below MPC. In other words, the very high decontamination possible with this process produces subsidiary waste streams which are essentially insignificant. Virtually all of the nuclides present in the original waste stream are included in the designated waste form.

CONSOLIDATION

The solidified wastes can be consolidated to obtain the highest thermal conductivity and minimize storage volume, dispersion potential and leachability. Prior to consolidation, numerous characterization studies, including particle size determinations,

SANDIA SOLIDIFICATION PROCESS

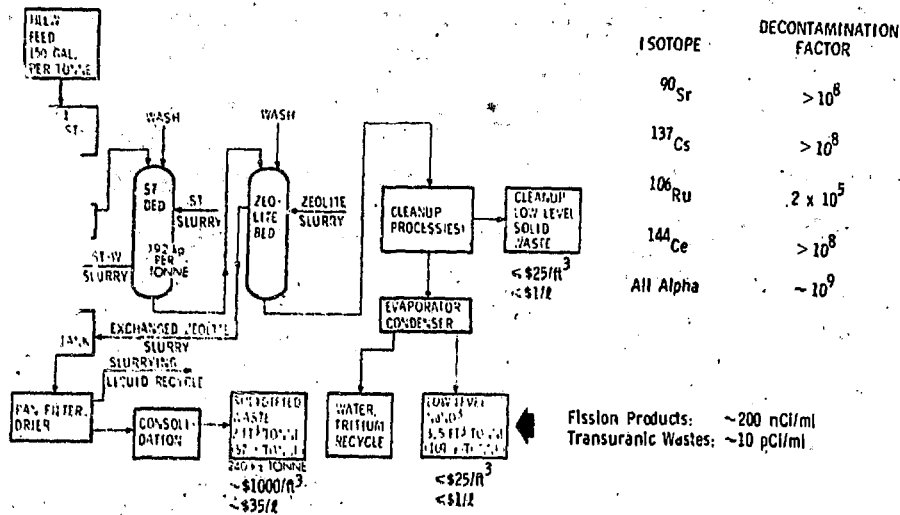


Figure 1: Simplified flow diagram describing the Sandia Solidification Process for nuclear waste solidification. A table of decontamination factors is also shown.

surface-area measurements, differential thermal analysis, and thermogravimetric analysis, were performed on the exchanged materials in order to better understand their behavior during consolidation. The first consolidation method evaluated was cold pressing and sintering; however, poor relative densities were obtained. Vacuum hot pressing in graphite dies was successful from the start. Hot pressing was particularly attractive compared with atmospheric sintering because of the lower temperature required to obtain an equivalent densification, the shorter residence times at maximum temperature, close dimensional control of the final billet and small-grained microstructure. This last point is particularly important in that the effects of alterations in individual phases on the compact as a whole is minimized.

The remainder of the consolidation program was aimed at optimizing the hot-pressing parameters and studying the effects of material variables on the final product. The hot-pressing parameters studied included pressure (1-165 MPa), heating

rate (15-100°C/min), maximum temperature (900-1200°C), soak time (0-4 hours), sample size (3/8-2 in. dia), and atmosphere (vacuum or argon). Material variables included waste composition (Si, zeolite, unreacted "titanate" and residual Na content), variations between different batches of exchange material, glass binder additions and precalcination of the exchanged feed material.

As shown by the relative density/temperature plots in Figure 2, full density pellets were obtained regardless of the variations in the material parameters. The optimum hot-pressing conditions for pellets up to 2 in. in diameter were:

Heating rate:	35°C/min
Pressure:	4-7 MPa (600-1000 psi)
T _{max} :	1100°C
Residence time at T _{max} :	10 min

The total time above 700°C is about 40 minutes. These conditions are quite mild with respect to those required for hot pressing most ceramics.

THERMAL/PHYSICAL PROPERTIES

Typical properties of the consolidated wastes are given in Table 1. Densities of unaltered (no glass binders) wastes ranged from 4.1 to 4.3 g/cm³. The residual porosity was usually less than 1 vol%. The effective density of waste oxides was 0.9 to 1.1 g/cm³. The residual porosity was usually less than 1 vol%. The effective density of waste oxides was 0.9 to 1.1 g/cm³. The thermal properties up to 1000°C were determined. The thermal conductivity of the titanate waste is about twice that of borosilicate glass; consequently for equivalent waste oxide density and canister size, the dense titanate waste should exhibit a significantly lower storage temperature.

The thermal stability measurements listed in Table 1 were run on hot-pressed pellets, not powders--hence the data for dimensional change. The data are total values relative to time = 0. For example, a total weight gain of 0.34% was observed after 475 hours at 800°C. The weight gain is due to the reoxidation of the samples

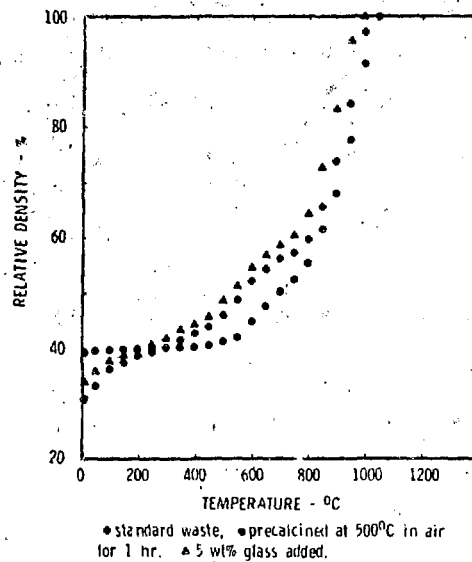


Figure 2. Relative Density/Temperature Plots Showing the Effects of Selected Variables on the Consolidation Behavior of Titanate Wastes by Hot Pressing.

Table 1

PROPERTIES OF PRESSURE-SINTERED TITANATE RADWASTE

(ST-W + 2% Si + 10% Zeolite)

Bulk density	4.1-4.3 g/cm ³
Volume fraction porosity	0.03
Weight fraction waste oxides	0.22-0.25
Effective density of waste oxides	0.9-1.1 g/cm ³
Thermal conductivity (at 400°C)	0.0066 cal/cm sec K
Specific heat (at 400°C)	0.22 cal/g K
Thermal stability (800°C in air)	

	ΔWeight	ΔVolume
	%	%
210 hours	+ 0.32	+ 4.62
475 hours	+ 0.34	+ 5.85

which were reduced during hot pressing. Examination of the microstructure following the 475 hour test revealed the development of microcracks in a surface layer which was about 200 μm thick. Quantitative microprobe studies of the surface layer show a decrease in the Cs and Rb content and an increase in the Na content. The concentration of the rest of the cations appear relatively unaffected.

LEACH BEHAVIOR

The leach results for the complete titanate waste and zinc boro-silicate glass are given in Table 2.

Table 2

SOCHLET LEACH RESULTS

Bulk Samples

$\sim 95^\circ\text{C}$

	<u>Mass loss - $\mu\text{g/g}$</u>			
	<u>Cs</u>	<u>Mo</u>	<u>Sr</u>	<u>Total</u>
Week 1				
STW	ND*	18	ND	70
SLA glass	90	43	16	1460
PNL glass	ND	12	2	310
Week 3				
STW	ND	21	ND	66
SLA glass	11	96	4	2320
Month 2				
STW	ND	12	22	267
SLA glass	170	266	62	11330
PNL glass	1	68	3	3493
Month 3				
STW	ND	18	2	89
SLA glass	269	138	195	7421
PNL glass	9	56	5	1320

These tests were run in a Soxhlet apparatus at $\sim 95^{\circ}\text{C}$. All of the samples were in bulk form rather than crushed. Two zinc borosilicate glasses were tested simultaneously with the titanate waste. One of the glasses (SLA glass) was fabricated at Sandia according to the Pacific Northwest Laboratories' (PNL) recipe (73-1 frit). Twenty-five weight percent PW-7 simulant was added to the frit which was melted and cast into plates. A piece was cut from the plate for leach testing. A glass obtained from PNL (PNL glass three weeks after the tests had begun; consequently the PNL glass has been leached three weeks less than the other two samples. The surface areas are approximately equal, hence the results are given in grams of cation leached/gram of total sample.

There are several interesting results so far in these on-going tests. There is a rather wide range of leach values covered by the two identical glasses. These results are probably within normal scatter. Both glasses have developed a dull coating which can be rubbed off (but has not been). The titanate ceramic so far shows excellent results with one exception--the appearance of Sr during the fourth week. Note that in the third month the Sr leachability has dropped off significantly, suggesting a transient behavior of some kind. The behavior is disturbing because the mechanism controlling this effect is unknown. However, such results accent the need for detailed, comprehensive long-term leach tests on any waste form.

MICROSTRUCTURAL AND PHASE CHARACTERIZATION

Considerable effort was directed toward microstructural characterization and phase identification in the consolidated ceramic. Studies have included optical microscopy, transmission electron microscopy, electron microprobe analysis, energy-dispersive analysis, selected-area electron diffraction, and x-ray diffraction.

A typical microstructure for a hot-pressed titanate waste is shown in Figure 3. The complex titanate waste matrix (A) contains irregular amorphous zeolite regions (B) and metallic particles of silicon (C) which are surrounded by amorphous SiO_2 (D). A small amount of residual porosity (E) is present which is usually associated with one of the phases containing SiO_2 . The titanate matrix is totally unresolved at these

magnifications. The only phase identifiable by x-ray diffraction techniques was rutile, the primary phase. Several lines associated with an unknown phase(s) were also observed.

Scanning transmission electron microscopy (STEM) was initiated in an attempt to resolve the titanate microstructure and identify additional phases. STEM has become an important tool in our microstructure characterization effort. With this instrument, selected-area electron diffraction (SAD) can be performed on individual crystallites on the order of 200Å in size. Selected-area diffraction permits observation of phases which are too small or in too low a concentration for x-ray diffraction studies. A transmission electron micrograph of the hot-pressed titanate waste along with a list of phases identified by SAD are given in Figure 4. The micrograph shows the extremely small and varied morphology of the crystallites in the waste matrix. The lattice parameter has been determined for several phases which have not been identified. The phase assemblage appears to be quite stable. Grain growth is limited by the large number of different phases in the matrix. Even regions of pure rutile show limited grain growth due to precipitate pinning of the grain boundaries. STEM studies of waste heat-treated to 1200°C for 24 hours show only slight grain growth and no detectible phase change.

Selected binary and ternary titanate systems have been prepared for on-going x-ray diffraction studies in an attempt to further unfold the complex phase relations. Current results confirm the presence of elemental Pd. U and Ce do not form titanates when no other cations are present. These systems contain rutile with U_3O_8 and CeO_2 respectively. The Gd_2O_3 - TiO_2 system yields rutile and $Gd_2Ti_2O_7$. The Nd_2O_3 - TiO_2 system yields rutile and $Nd_2Ti_3O_{8.7}(?)$ plus an additional unidentified phase (possibly based on the Na impurity). The $Nd_2Ti_3O_{8.7}$ diffraction pattern appears to account for the unidentified lines obtained from the hot-pressed waste discussed above.

SUMMARY

The Sandia Solidification Process offers a unique approach to reactor waste solidification. It is a simple process which effectively removes virtually all

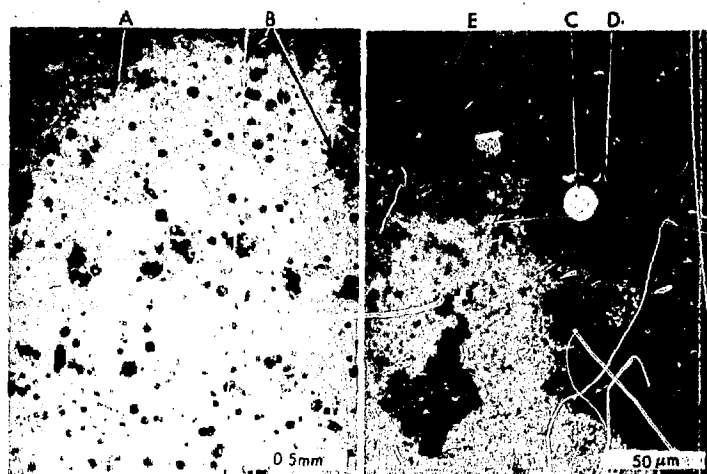


Figure 3. Microstructure of Hot-pressed Titanate Waste Showing: (A) Titanate Matrix, (B) Amorphous Zeolite Regions (C) Metallic Si Particles (D) Amorphous SiO_2 Coatings and (E) Residual Porosity.



PHASES IDENTIFIED IN TITANATE WASTES

Phase	Additional Ions in the Phase
TiO_2 (rutile)	--
SiO_2 (amorphous)	U, Al, Na
$\text{Cs}_2\text{O} \cdot \text{Al}_2\text{O}_3 \cdot 4\text{SiO}_2$ (pollucite)	Rb
$\text{Gd}_2\text{Ti}_2\text{O}_7$	U, Zr, Y, Sm, Eu
Mo (elemental)	Fe
Pd (elemental)	Te, Fe, Mo, U
ZrO_2 (cubic)	U, Si, Y

Figure 4. Transmission Electron Micrograph Showing Complex Microstructure of the Titanate Matrix and a List of Phases Identified by Selected-Area Diffraction.

cationic species from a reactor waste stream, and can also remove selected isotopes for beneficial applications. Various separation and partitioning studies are currently in progress. Following a waste solidification application, the solid waste can be easily consolidated using hot-pressing techniques into an apparently stable but complex ceramic waste form. The entire process has been successfully demonstrated with fully radioactive reactor wastes. Characterization studies have shown the detailed structure of the final waste form and its thermal/chemical behavior to be complex. These results suggest that detailed characterization studies are necessary for any waste form and that extreme care must be taken when extrapolating data to long times.

CNF-57012--2

THE RETENTION OF REACTOR PRODUCTS IN THE OKLO NATURAL FISSION REACTOR

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THE OKLO PHENOMENON

Within the past few years it has been clearly demonstrated that a series of natural fission reactors operated nearly 2×10^9 years ago in rich uranium ore deposits located in the Oklo mine in the southeast part of the Republic of Gabon, West Africa (1, 2, 3, 4). Four separate reactor zones have been identified, all in the same part of the open-pit mine. They operated over a period of about 600,000 years. During this time 15000 MW-years of energy was generated at an average level of 25 KW. Approximately six tons of U-235 were consumed, creating an equivalent amount of fission products deposited directly in the ground. Nearly three tons of Pu-239 were created by neutron capture on U-238 which eventually decayed quantitatively to U-235. Approximately one thousand tons of uranium were involved in the reaction zones.

These zones were highly enriched lenses of uranium ore, averaging over 20% in uranium content within an ore body of about 0.5% average concentration. At the time of criticality the initial atomic ratio of the fissionable U-235 isotope was 3%. The rich lenses were highly irregular in form but tended to be tabular, about one meter thick, and several hundred square meters in area. Following initial deposition in fluvial sediments and subsidence, the formation was tilted about 45° and faulted. The rich ore zones then formed in structural traps and, presumably, achieved criticality as soon as a high enough uranium concentration was reached in the presence of the transporting and neutron-moderating medium, water.

REACTOR PRODUCT RETENTION

The fact that nature and not man had designed the first terrestrial fission reactor was, at least initially, surprising. Perhaps even more surprising was the remarkable state of preservation of the reactor. Quantitative and semi-quantitative analyses for the various reactor products showed that the majority of them had been retained. It was also possible to demonstrate that the reactor zones had preserved their initial geometries, i.e., the ores had not undergone physical or chemical mixing. The arguments which support these conclusions are presented in detail in the Proceedings of the Oklo Symposium and only the conclusions are summarized here. The degree of retention of the principal reactor products is summarized in Table 1 (5).

From microscopic and heavy-ion stimulated ion-emission studies (6, 7) a great deal has been learned of the composition of the ore and the location of the reactor products. Although the uranium outside the reactor zones in low concentration ores is largely pitchblende, the mineral in the highly enriched reaction zones is generally uraninite in the form of grains, of the order of 40-200 μm in diameter, distributed in a phyllitic gangue (chlorite plus illite). These analyses show that there is always associated with the uraninite grains some calcium, fluorine, sodium, titanium, rare earth fission products, zirconium, ruthenium, palladium, yttrium, lead, and thorium. In the gangue one finds boron, lithium, potassium, much of the radiogenic lead, barium, strontium, and some of the fission product zirconium and ruthenium. The ratio of U-235 to U-238 appears to be constant in the uraninite grains. The fact that none of the U-235 is outside the grains leads to the conclusion that the large amounts of Pu-239 formed by neutron capture on U-238 decayed within the uraninite grains to U-235.

Additional analytical results are available from samples taken as closely as every 2.5 cm in traverses across the reactor zones (8, 9). These show generally consistent agreement between depletions in the U-235 abundance, neutron fluences evaluated from second-order neutron capture effects in the rare earths, absolute

Table 1
MIGRATION OF FISSION PRODUCTS AND ACTINIDES IN THE
"ZONE 2" REACTOR AT THE OKLO MINES

Element	Migration Behavior	References
Kr	Measurable traces, 0.01 to 1% remaining	12,13,15
Rb	Measurable traces, less than 1% remaining	13,14,16,17
Sr	Measurable traces, less than 10% remaining	13,16,17
^{90}Sr (Now ^{90}Zr)	Small migration, most decayed in place	15,16
Zr	Redistributed, mostly in place	7,15,16
Nb	Mostly retained	13,15
Mo	~ 90% missing	13,15,16
^{99}Tc (Now ^{99}Ru)	Redistributed, migrated as Tc	15,16
Ru	Large fraction retained, redistributed	13,15,16,19
Pd, Ag	Mostly retained	13,15
Cd	~ 90% missing	13,18
Te	Mostly retained	13,15
I	Mostly gone	13,15
Xe	Measurable traces, 0.01 to 1% remaining	13,15,16
Cs	Measurable traces (as Ba), mostly missing	13,15,17
Ba	Obscured by natural but mostly gone	13,15,16
Ce, Nd, Sm, Gd	Very little migration	9,13,15,16,19,22
Pd	Redistributed, ~ 2/3 missing from core	7,13,20,21
^{232}Th (^{236}U , ^{240}Pu)	Mostly retained	9,15
^{209}Bi (^{237}Np , ^{241}Pu)	Mostly retained	9,15
^{235}U (^{239}Pu)	No ^{239}Pu separation from ^{238}U	7,13
U	Probably no major migration some redistribution, (see text)	9,13,15,22

rare earth fission product concentrations, and uranium concentrations. Although in some traverses there is evidence that a part of the uranium has been lost from regions near the outside of the reactor zones (or that rare earth fission products have been gained), in general the ratio of neodymium to uranium has been quantitatively preserved even on a scale of centimeters. These observations are consistent with the microscopic observations that the neodymium has been quantitatively retained within the original uraninite grains. Taken together, they support the conclusion that there has been no extensive geochemical or geophysical mixing of the uraninite grains.

The apparent stability of the grains of uraninite demonstrated by these observations seems particularly remarkable because even rather small changes in pH and Eh, especially if accompanied by an increase in dissolved carbonates, can lead to rapid oxidation and dissolution in the form of a uranyl double carbonate or, at least, to the formation of secondary, oxidized minerals of uranium (10). The observed stability cannot be attributed to the absence of exposure of the ore to moving ground-water. The reactor ore was deposited by water and the neutron reaction required water to achieve criticality. The most soluble fission products have been almost quantitatively removed or replaced. Age measurements show that two-thirds of the total radiogenic lead has been lost which means that exposure to water occurred over a large part of the life of the ore-body or re-occurred in relatively recent times. Accordingly, it appears evident that water was present but must have been buffered within a narrow pH and Eh range.

Self-buffering of ground water, even at rather shallow depths in a reasonably large volume of a given soil type, is probably the rule rather than the exception (11). Thus, the Oklo observations support the conclusions that, despite the extreme vulnerability of a mineral such as uraninite to geochemical attack and dissolution, it can retain its integrity and composition to a remarkable degree over billions of years while immersed in natural ground-water. Given the variation in measurements

within the reactor zones, we estimate that the transport of uranium out of the principal reactor zones averaged no more than 20% in the most affected regions. This means that the fractional loss of uranium was no more than 10^{-10} per year. The hydrological and geological conditions which were responsible for this degree of stability are probably not uncommon.

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MATERIAL PROPERTIES

THE STABILITY OF GLASSES, WITH SPECIAL REFERENCE
TO THE DISPOSAL OF RADIOACTIVE WASTES

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The stability of glasses is considered with reference to their possible use in the disposal of radioactive wastes. The stability of glasses against devitrification is seen to depend on kinetic factors which determine the rates of nucleation and crystal growth. In the range of large undercoolings relevant to the problem of waste disposal, homogeneous nucleation seems to represent the dominant contribution to the formation of crystals; and the need of further investigations of such nucleation in glass-forming systems is indicated. Crystal growth in the complex compositions of interest will very likely be diffusion-controlled. The need of improved theoretical descriptions of such growth, together with additional data on and better insight into the interdiffusion coefficient in complex systems, are indicated. The phenomenon of phase separation is seen to be widespread in glass-forming systems, and can have a profound effect on the properties and transformation behavior of glasses. Consideration of this phenomenon should be included in any formulation of glasses for the disposal of radioactive wastes.

INTRODUCTION

The present paper will be concerned with the structure and stability of glasses. Particular attention will be directed to oxide glasses for possible use in the disposal of radioactive wastes. The question of stability--or the lack of it--is inherent in the very notion of a glass. Thermodynamically, glasses represent unstable (or perhaps metastable) structures, which persist for long periods

of time only because the kinetics of rearrangement to the crystalline forms are slow.

The persistence of thermodynamically metastable phases for long periods of time should be familiar to all. Although one frequently hears in advertisements that "diamonds are forever," it is well established that under ambient conditions the stable form of carbon is graphite; and given sufficient time (perhaps measured in millenia), diamonds will transform to graphite. Despite this, few people are hesitant about buying diamonds because of their instability. In the case of typical glasses, the kinetic barrier to crystallization is smaller than that involved in the diamond-graphite solid-state phase transformation; and the role of water in serving as a mineralizer and increasing the kinetics of crystallization of silicate glasses is well known. Because of the mineralizing effect of water, which often involves dissolution of the glass into the hydrous phase and subsequent crystallization from this phase, the oldest known terrestrial glasses--such as those found in a number of lava flows and rhyolite cliffs--are much younger than many glasses returned from the anhydrous lunar surface, which have persisted as glasses for more than a billion years. By comparison, the "old" terrestrial glasses have existed as amorphous solids for some 35 millions years.

It is widely believed that glasses can be formed of nearly any liquid if it is cooled sufficiently rapidly to a sufficiently low temperature without the occurrence of detectable crystallinity. On this basis, the question to be asked in considering glass formation is not whether a material will form a glass but rather how fast must a material be cooled in order to obtain a glass. This has led to kinetic approaches to glass formation, which will be discussed in the following section.

KINETIC TREATMENT OF GLASS FORMATION

The treatment used to describe the conditions needed to form a glass of a given material is also useful for describing the resistance of a glass to subsequent crystallization (devitrification). In the case of glass formation, it is useful (1, 2, e.g.) to identify a volume fraction crystallized (V_c/V) of 10^{-6} as a just-detectable degree of crystallinity and employ the formal theory of transformation kinetics (3, e.g.) to evaluate the time required at a given temperature for this degree of crystallinity to form. In the frequently-encountered case where the rates of crystal growth and nucleation are constant with time, the volume fraction crystallized in a time, t , can (for small V_c/V) be expressed:

$$V_c/V \approx \frac{\pi}{3} I_v u^3 t^4 \quad (1)$$

where I_v is the nucleation frequency per unit volume and u is the growth rate.

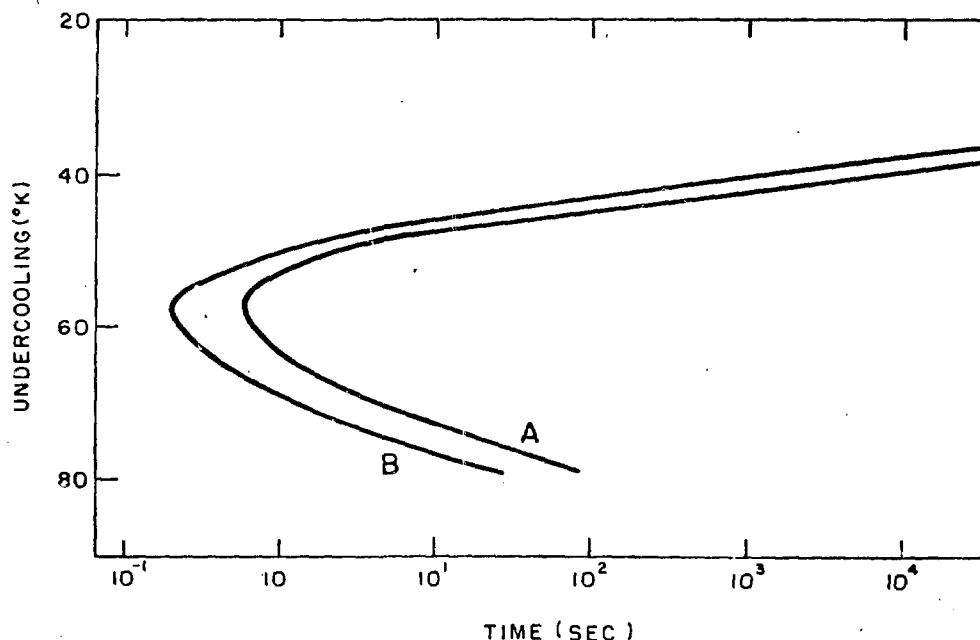


Figure 1. - Time-temperature-transformation curves for salol corresponding to volume fractions crystallized of 10^{-6} . After D. R. Uhlmann, J. Non-Cryst. Solids 7 (1972) 337.

The cooling rate required to avoid a given fraction crystallized can be estimated from Eqn. (1) by constructing time-temperature-transformation (TTT) curves corresponding to the given V_c/V . Examples of TTT curves for salol are shown in Fig. 1 for two different volume fractions crystallized. These curves are constructed by calculating the time required for the given V_c/V to form at a particular temperature (using values of I_v and u), and repeating the calculation for other temperatures. As expected from the form of Eqn. (1) and as shown by the curves in Fig. 1, the time required to reach a given fraction crystallized does not depend strongly on the assumed volume fraction crystallized.

The critical cooling rates necessary to avoid the given fraction crystallized--and hence to form a glass--can be obtained by the construction (2) of continuous cooling curves. These curves are constructed from the isothermal TTT curves following the approach of Grange and Kiefer (4). The curves describing crystallization during continuous cooling indicate that a given degree of crystallinity is developed at lower temperatures and longer times than a cursory examination of the isothermal TTT curves or Eqn. (1) would suggest.

On this basis, evaluation of the critical conditions for glass formation reduces to an evaluation of the nucleation frequency and the growth rate. When appropriate data are available, measured values of the growth rate should be employed. For liquids which crystallize without a change of composition, u can often be calculated from the relation:

$$u = \frac{f_s K_u}{\eta} \left[1 - \exp \left(- \frac{\Delta H_f \Delta T_r}{RT} \right) \right] \quad (2)$$

Here f_s is the fraction of preferred growth sites on the interface; $K_u \approx 10 \text{ cm sec}^{-1}$ poise; η is the viscosity; ΔH_f is the molar heat of fusion; and $\Delta T_r = \Delta T/T_M$, where ΔT is the undercooling ($\Delta T = T_M - T$) and T_M is the melting point.

For materials with small entropies of fusion ($\Delta H_f/T_M < 2R$), $f_s \approx 1$; while for materials with large entropies of fusion ($\Delta H_f/T_M > 2R$), $f_s \approx 0.2 \Delta T_r$ (5, 6).

Data on nucleation frequency are seldom available; and it is usually necessary to estimate I_v from theoretical models. By taking I_v as the rate of homogeneous nucleation, one can estimate the MINIMUM conditions for glass formation, since if a material will not form a glass at a particular cooling rate when nucleating heterogeneities are absent, it will certainly not form a glass when such heterogeneities are present. For homogeneous nucleation, I_v in Eqn. (1) is generally taken as the steady-state nucleation rate:

$$I_v \approx \frac{K_I}{n} \exp(-B/T_r^3 \Delta T_r^2) \quad (3)$$

The constant B in the numerator was originally (1) taken as 1.024, corresponding to a free energy of forming the critical nucleus (ΔG^*) of 50 kT at $\Delta T_r = 0.2$, based on the results of droplet nucleation experiments on a variety of simple liquids. Subsequent work on silicate systems, to be discussed below, suggests that somewhat larger values of B--in the range of 1.13 to 1.23--are often more appropriate.

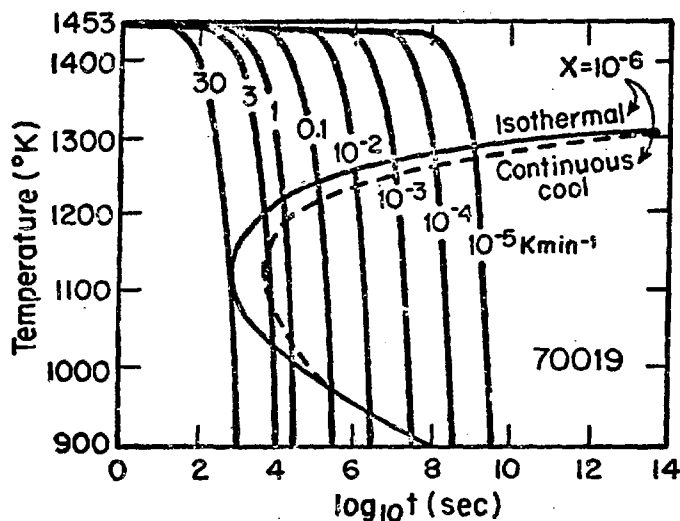


Figure 2. Isothermal TTT and continuous cooling curves for lunar composition 70019. $V_c/V = 10^{-6}$. After D. R. Uhlmann, L. Klein, P.I.K. Onorato and R. W. Hopper, pp. 579-593 in Proceedings of the Sixth Lunar Science Conference, Vol. 1 (Pergamon Press, New York, 1975).

An example of isothermal (TTT) and continuous cooling (CT) curves for a just-detectable degree of crystallinity of 10^{-6} are shown in Figure 2 for lunar composition 70019. This material has the following composition (in wgt. pct): SiO_2 , 41.3; TiO_2 , 8.4; Al_2O_3 , 12.4; FeO , 16.1; MgO , 10.21; CaO , 11.2; and Na_2O , 0.3. The isothermal TTT curve was constructed (7) from growth rate and viscosity data on this composition, assuming $\Delta G^* = 60 \text{ kT}$ at $\Delta T_r = 0.2$. The CT curve was constructed from the TTT curve following the method in (4). The critical cooling rate required to make a glass of this material is estimated from Figure 2 as about 4 K min^{-1} .

The greatest uncertainty in the treatment is its evaluation of the nucleation frequency. The effects of variations in the nucleation barrier are illustrated by Figure 3, where TTT curves are shown for anorthite ($\text{CaO} \cdot \text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2$) for $\Delta G^* = 50 \text{ kT}$, 60 kT and 70 kT at $\Delta T_r = 0.2$. The corresponding minimum cooling rates for glass formation are: 3×10^3 , 3×10^2 and 40 K sec^{-1} .

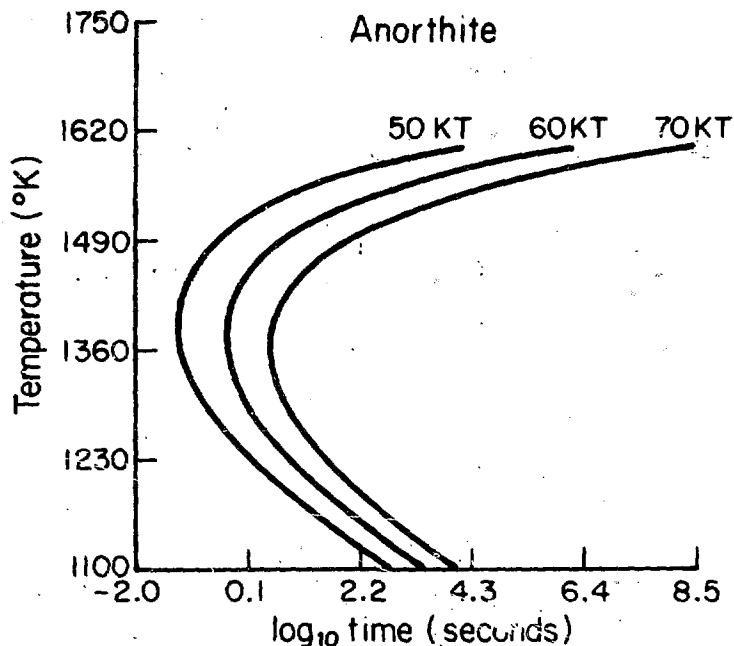


Figure 3. Time-temperature-transformation curves for anorthite corresponding to nucleation barriers at $\Delta T_r = 0.2$ of 50kT, 60kT and 70kT. $V_c/V = 10^{-6}$. After P.I.K. Onorato and D. R. Uhlmann, J. Non-Cryst. Solids 22 (1976) 367.

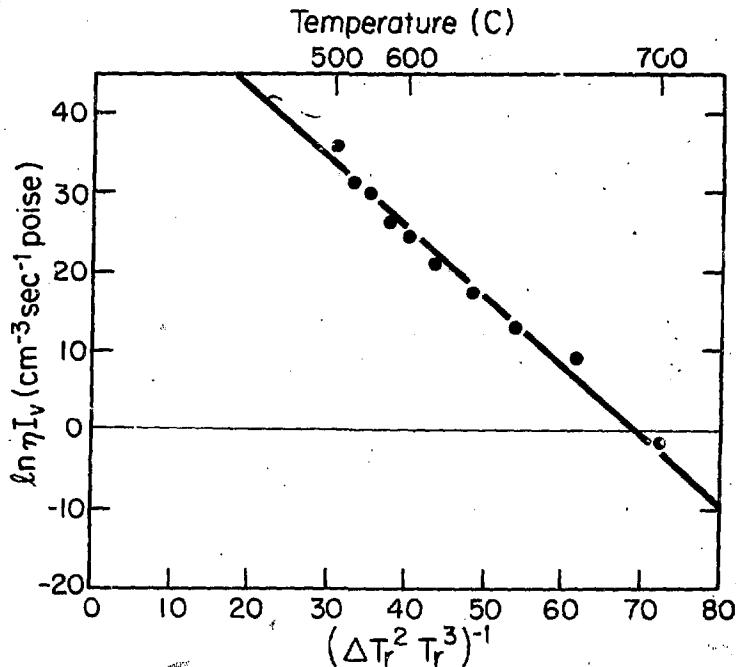


Figure 4. Variation of $\log$ (nucleation rate times viscosity) versus $1/\Delta T_r^2 T_r^3$ for lunar composition 70019. After L. Klein and D. R. Uhlmann, pp. 1113-1122 in *Proceedings of the Seventh Lunar Science Conference, Vol. 1* (Pergamon Press, New York, 1976).

Direct measurements of nucleation rates in glass-forming systems have been difficult to accomplish because the familiar droplet technique cannot conveniently be used. Such rates have, however, recently been measured in our laboratory (8, e.g.) using Eqn. (1) together with measurements of the growth rate and the time required at various temperatures to form sensibly-crystalline bodies. The nucleation frequencies determined in this way for lunar composition 70019 are shown in Figure 4. According to Eqn. (3), the $\ln(I_v \eta)$ vs $1/\Delta T_r^2 T_r^3$ relation should be a straight line of negative slope; and such a straight line is indicated by the data in Figure 4. The slope of the least squares line through the data indicates a nucleation barrier of about 55 kT at $\Delta T_r = 0.2$; and the intercept at $1/\Delta T_r^2 T_r^3 = 0$ corresponds to a value of $5 \times 10^{33} \text{ cm}^{-3} \text{ sec}^{-1} \text{ poise}$. The latter value is in excellent agreement with

predictions (9) of the classical theory of homogeneous nucleation ($K_1 \approx 10^{30} \text{ cm}^{-3} \text{ sec}^{-1} \text{ poise}$).

One further result of the study seems particularly germane to the question of the stability of glasses used in the disposal of radioactive wastes. This is the finding that over the range of large undercoolings ($\Delta T > 250^\circ\text{C}$), homogeneous nucleation represents the dominant contribution to the formation of crystals, and nucleation on heterogeneities present in the melt can effectively be neglected. If this result is general, it suggests that a determination of B in Eqn. (3) for glasses of interest--or the development of ability to predict its value--should be an important part of the development program on glasses for waste disposal.

The effects of nucleating heterogeneities on glass formation have been evaluated (10) using a kinetic treatment of the type outlined above together with the familiar spherical cap model of the heterogeneous nucleus. The results indicate that while heterogeneities with contact angles less than 180° are properly described as nucleating heterogeneities, only those with contact angles less than about 100° have a significant effect on glass-forming ability, at least for the concentrations of heterogeneities usually found in liquids. For heterogeneities with small contact angles, the effect in increasing the critical cooling rate for glass formation can be substantial.

The usual experience with glass-forming liquids is that crystals nucleate preferentially at external surfaces, and at the surfaces of internal heterogeneities. Such nucleation is usually associated with condensed second-phase particle. Nucleation at external surfaces can be reduced, and the stability against crystallization increased, by fire polishing the surfaces or by chemical etching and by taking care not to touch the surfaces subsequent to such treatments. Nucleation at external surfaces often gives rise to a columnar crystallization morphology, with relatively poor mechanical properties and inadequate chemical durability.

The ability to produce many internal nuclei in glass-forming liquids by the addition of selected nucleating agents is important in forming glass-ceramic materials, as well as glazes and enamels with desired degrees of crystallinity. Such controlled internal nucleation can produce microstructures with a high degree of uniformity and with improved mechanical properties. For the case of present interest, disposing of radioactive wastes, it seems important to obtain either: (a) highly crystalline bodies by controlled crystallization (and hence controlled nucleation); or (b) glassy bodies by avoiding the incorporation of heterogeneous nuclei in the melt and by selecting compositions which are relatively resistant to crystallization. Other papers at this Workshop indicate the presence of relatively refractory crystalline heterogeneities in many of the glasses now being considered for use in waste disposal. For producing glasses, but not necessarily for producing bodies with outstanding resistance to subsequent devitrification (see above), such heterogeneities should be eliminated--perhaps by the use of systems containing sizable concentrations of FeO or PbO, which serve as fluxes.

Besides the nucleation rate, the other factor which determines the resistance of a body to crystallization is the growth rate. The best understanding in this area has been developed for systems which crystallize without a change of composition--i.e., single-component materials or congruently-melting compounds. For such materials, studies of glass-forming systems have been useful in elucidating the nature of growth from the melt (see review in Ref. 11).

In the world of commercial glasses and the glasses likely to be used in the disposal of radioactive wastes, one deals with systems which are compositionally complex. Such compositions can be likened to a garbage dump, with a pile of this and a heap of that used to optimize properties and to increase resistance to crystallization.

Such materials are characterized by sizeable changes of composition on crystallization. The most studied system in this regard is the familiar $\text{Na}_2\text{O}-\text{CaO}-\text{SiO}_2$ system over a range of compositions near that of the familiar window glass or bottle glass. The growth of the crystalline phase, devitrite ($\text{Na}_2\text{O} \cdot 3\text{CaO} \cdot 6\text{SiO}_2$), proceeds at a rate which is independent of time until crystallization is largely complete. The variation of growth rate with temperature for a composition in this system is shown in Figure 5. The curve in Figure 5 illustrates the familiar maximum growth rate found in glass-forming systems. The maximum results from a competition between the driving force for crystallization, which increases with increasing undercooling, and the molecular mobility, which decreases with increasing undercooling. To illustrate the effects of impurities on growth rate, it was found that additions of Al_2O_3 decreased the growth rate, as did the substitution of Mg for Ca.

For systems whose crystallization involves large compositional changes, one might expect that growth rate to be diffusion-controlled and decrease as the square root of time. Observations on many systems including $\text{Na}_2\text{O}-\text{CaO}-\text{SiO}_2$ indicate growth rates which are independent of time. Examination of the growth morphologies in these cases have provided insight into the behavior. These morphologies often take the form of closely-spaced arrays of fibrils or dendrites. For such structures, diffusion-controlled growth takes place at rates which are independent of time (12, 13, e.g.); and descriptions of this growth must direct attention to the effects of overlapping diffusion fields.

Progress has been made in developing models for predicting the growth rate from other measurable quantities (14, 15, e.g.). The theoretical models developed to date are relatively simple; and it seems important to obtain experimental data on a number of systems, even relatively simple two-component systems, to serve as a guide for development of improved theoretical descriptions. The test of these and improved models will require data on parameters such as growth rate, interdiffusion coefficient, dendrite radius and dendrite spacing--which are not presently available.

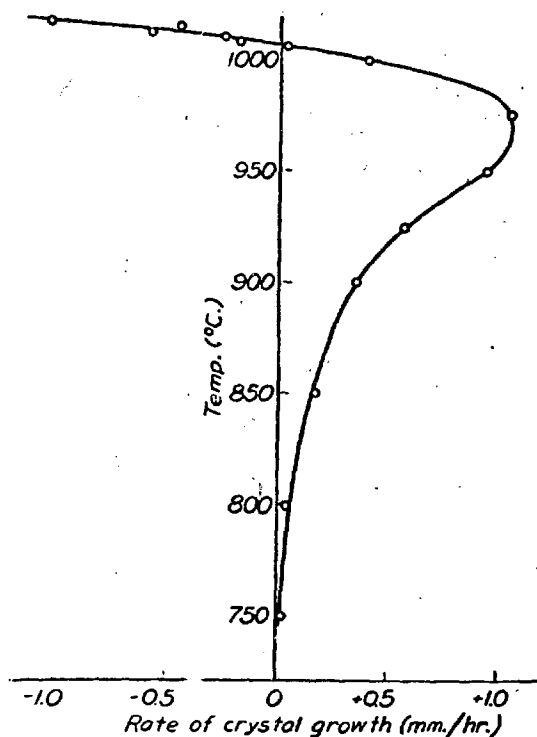
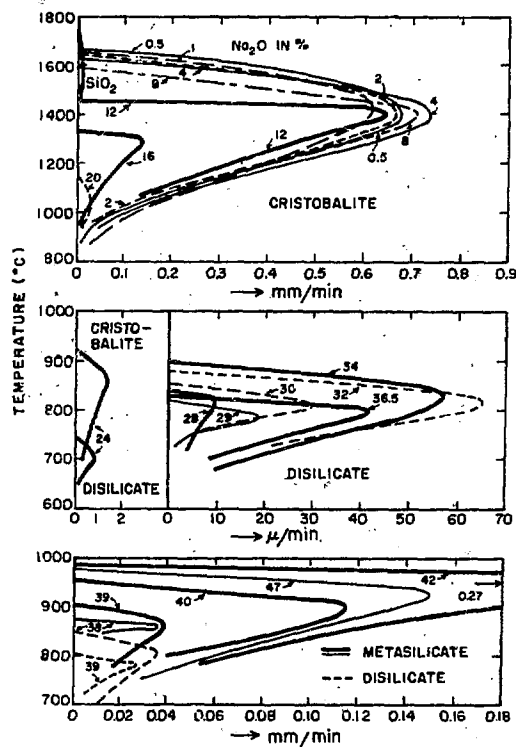


Figure 5. Variation with temperature of the growth rate and dissolution rate of devitrite crystals in a $\text{Na}_2\text{O}-\text{CaO}-\text{SiO}_2$ melt. After H. R. Swift, J. Am. Ceram. Soc. 30 (1947) 165.

Figure 6. Variation of growth rate with temperature for various compositions in the $\text{Na}_2\text{O}-\text{SiO}_2$ system. After A. Dietzel and H. Wickert, Glastechn. Ber. 29 (1956) 1.



Even with improved descriptions of growth, it will be important to obtain data on the interdiffusion coefficient; and such data are generally available for complex silicate systems.

With increasing undercooling, the scale of the crystallization morphology generally becomes finer; and at very large undercoolings, the transition to a spherulitic morphology is often observed. The nature of this transition in morphology, and indeed the characteristics of spherulitic growth quite generally, are poorly understood. This subject has important implications in a variety of areas besides the disposal of radioactive wastes, including importantly the crystallization of many polymers.

The effects of composition on growth rate are shown in Figure 6 for the $\text{Na}_2\text{O-SiO}_2$ system. The smallest growth rates in this and many other systems are observed in near-eutectic regions. Such low growth rates are expected because of the transport of solute required for crystallization and also because of low liquid temperatures in these regions.

The effects of melting point or liquidus temperatures on the conditions required to form glasses of different materials are shown in Figure 7 for materials having the same viscosity-temperature relation, entropy of fusion and other properties as $\text{Na}_2\text{O} \cdot 2\text{SiO}_2$, but with assumed melting points of 1046°K, 1146°K (the actual melting point) and 1246°K. The minimum cooling rate required to form a glass of the material with $T_M = 1246^\circ\text{K}$ exceeds that for the material with $T_M = 1046^\circ\text{K}$ by 3 orders of magnitude. The effect of liquids temperature on glass formation is even more dramatic for lower-melting materials which have steeper viscosity-temperature relations.

For systems of possible interest in the disposal of nuclear wastes, there is a notable lack of data on phase equilibria. This lack hinders substantially the development of improved glasses for the application. For multi-year storage of wastes, it would seem necessary to maintain the system well below its glass transition temperature. While no data are available for crystallization in the range of the glass transition (T_g), the extrapolation of data obtained at higher temperatures suggests growth rates in the range of $100-1000 \text{ \AA}$ year at T_g .

Besides resistance to crystallization, consideration should also be directed to glass quality in designing systems for the disposal of radioactive waste. In this regard, specific attention should be directed to the problem of fining (the elimination of fine gas bubbles from melts) and homogenization (the development of glasses with only small variations in composition throughout the bodies). It is well established that composition can have a large effect on the rate of dissolution of glass in various media; and a highly homogeneous glass may dissolve much more slowly than a glass of the same average composition with large composition variations.

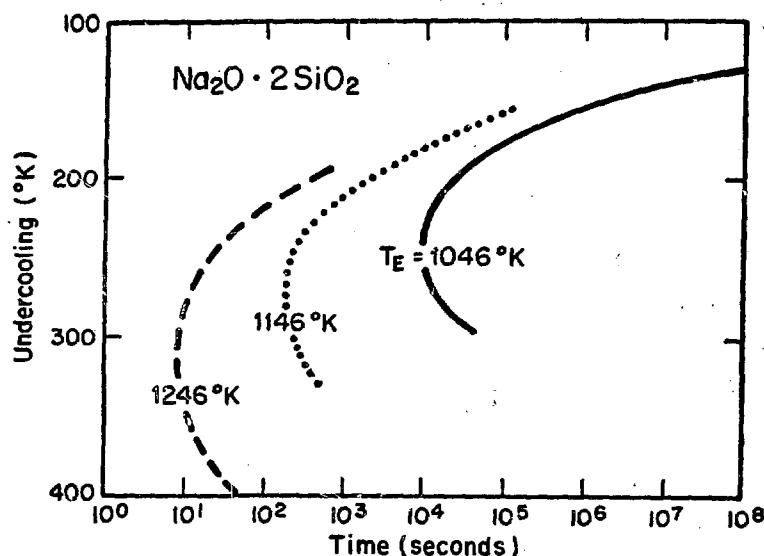


Figure 7. Time-temperature transformation curves for $\text{Na}_2\text{O} \cdot 2\text{SiO}_2$ -like materials with melting points of 1046°, 1146° and 1246°K. $V_c/V = 10^{-6}$. After D. R. Uhlmann: Proceedings of XI International Congress on Glass (Prague, 1977).

PHASE SEPARATION

Also important in discussing the stability of glasses is their tendency to separate into two amorphous phases. The discovery of this phenomenon has had a great impact on glass technology during the past two decades. On oxides alone, more than 200 papers were published in the area during the period 1970-1974, and several times this number appeared on other systems. The subject has been reviewed in a recent paper from our laboratory (16), and will be discussed only briefly here.

The separation of an initially single-phase liquid into two liquid phases is associated with the presence of miscibility gaps in the system. Such gaps can be stable or metastable, and have been observed in many glass-forming systems; and the possibility of phase separation must be included in considering the formulation, processing, properties and transformation behavior of glasses.

Phase separation can be observed on a scale of tens of Angstroms to thousands of Angstroms. When the scale is small, the glasses appear as optically homogeneous; but when the second-phase structures are larger than about 500-1000Å, pronounced scattering of light, producing translucent or opaque bodies, is usually observed. The morphology of separation may consist of discrete particles of one phase embedded in a second phase, or as structures in which both phases are three-dimensionally interconnected. Secondary phase separation is also frequently observed, in which either or both of the initially-separated phases becomes supersaturated on cooling and undergoes phase separation.

Composition has been shown to have a large effect on phase separation. Examples of compositional effects have been shown in a number of systems. Among such examples, the following might be noted: (1) the substitution of MgO for CaO in familiar soda-lime-silicate glasses decreases the temperature of immiscibility; (2) the addition of Al_2O_3 to compositions in the BaO-SiO₂ system has a pronounced effect in decreasing the temperature of immiscibility (for example, the addition of

as little as 2% Al_2O_3 can decrease the temperature of immiscibility by as much as 200°C); and (3) the addition of ZrO_2 , TiO_2 or P_2O_5 to typical silicate melts increases the temperature of immiscibility. In each case, the compositional range of immiscibility increases with increasing immiscibility temperature.

At the present time, there is no reliable way of predicting a priori the occurrence of miscibility gaps in most systems. Further, the very mechanism of phase separation in most systems under most conditions has yet to be established. Both discrete-particle and interconnected morphologies can arise either from spinodal decomposition or from nucleation and growth followed by coalescence. Theoretical descriptions of the phenomena have grown increasingly complex, and have included factors such as non-linear terms and thermodynamic fluctuations in spinodal decomposition and coalescence despite diffusional interference in nucleation-growth-coalescence.

The occurrence of phase separation affects nearly all properties of glasses. Changes in the softening point by more than 100°C and in viscosity at a given temperature by 5 orders of magnitude have already been demonstrated; and such phase separation can have a pronounced effect on the durability of glasses, both positively and negatively.

Phase separation can also have a profound effect on the process of crystal nucleation. In most cases of interest, this effect seems related to the formation of a phase of high molecular mobility, finely dispersed in a matrix phase which has desired characteristics in the crystallized state. The effects of phase separation on crystal growth are less pronounced than on nucleation, and should be most significant when the scale of separation is comparable with or larger than the scale of the growing crystals and their associated diffusion fields.

CONCLUDING DISCUSSION

The stability of glasses depends on kinetic factors which are also important in their initial formation--viz, on the kinetics of nucleation and crystal growth. Few studies of nucleation in glass-forming systems have been carried out to date. The limited available results indicate nucleation barriers in the range of those observed for other materials. Most nucleation events which occur at modest undercoolings reflect second-phase heterogeneities. Such nucleation often takes place at external surfaces, although internal nucleation on undissolved second-phase heterogeneities are also common. Based on the experience obtained in our laboratory on lunar compositions, it seems that for long times and low temperatures, which would be important for the stability of glasses used in the encapsulation of nuclear wastes, homogeneous nucleation should be the dominant nucleation processes.

The growth rate will depend on the particular system selected, but will likely be a diffusion-controlled kinetic process. Improved theoretical models of such growth--appropriate for complex silicate systems--are needed, as are more data to test these models and assist the development of improved theoretical descriptions. Among the data required are those on phase equilibria and interdiffusion.

In formulating glasses for the encapsulation of radioactive wastes, it seems important to develop "pig pen" compositions containing many components with properties tailored to the end use. Attention should specifically be directed to compositions with low liquidus temperatures, particularly those near eutectic compositions, since these should exhibit the greatest ease of glass formation and the greatest resistance to subsequent unwanted crystallization.

The phenomenon of phase separation is widespread in glass-forming systems. Such separation can have a pronounced effect on the properties and transformation characteristics of glasses, including their durability and their crystallization behavior. The possible occurrence of phase separation should be included in the formulation of any new glass composition.

Overall, one should be hopeful about the prospects for obtaining a glass for the disposal of radioactive wastes which will be stable for the desired period of time. Although the lunar environment is more favorable for glass stability than that of the earth, compositions have been returned from the moon which have existed as glasses for billions of years; and terrestrial glasses as old as 35 million years are known. If confidence is to be obtained in a "fix" for the disposal of radioactive wastes, however, significantly improved understanding of the basic kinetic processes important to glass stability will be required.

ACKNOWLEDGEMENT

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METAMICT MINERALS: ALTERATION AND RADIATION DAMAGE EFFECTS

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INTRODUCTION

The purpose of this discussion is to suggest that the study of metamict minerals may provide an insight into the long term stability of glass and crystalline phases, both in terms of alteration and radiation damage effects. Data on the alteration effects observed in metamict, rare-earth, AB_2O_6 -type Nb-Ta-Ti oxides will be summarized. Since much of this data has been published, it will not be repeated, but appropriate references will be cited. Structural controls on radiation damage in metamict minerals will be discussed with particular emphasis on the structure of the $ThSiO_4$ polymorphs, thorite and huttonite.

Metamict minerals belong to a special class of amorphous materials first described by Broegger (1). They are materials which are initially crystalline but which have become amorphous. Their properties have been summarized by Pabst (2). They are optically isotropic and amorphous to x-ray diffraction. Crystalline structures are reconstituted by heating, but the recrystallized phases may not include the original pre-metamict phase. Often complex phase assemblages form on heating (3). Compositions are complex and include U and Th (concentrations may be low, e.g., 0.41% ThO_2 in gadolinite). Although radiation damage from constituent U and Th nuclides almost certainly plays a role in the process of metamictization, it is a necessary but not sufficient cause, as some isochemical compositions exist in both the metamict and crystalline state (4, 5).

ALTERATION EFFECTS

The complex, orthorhombic, rare-earth, AB_2O_6 -type Nb-Ta-Ti oxides (A = REE, Pb^{+2} , Mn, Ca, Th, U, Pb; B = Nb, Ta, Ti, Fe^{+3}) include euxenite, polycrase, priorite, blomstrandine and aeschynite (6). All of these minerals occur in the metamict state and are often pervasively altered (7, 8).

The alteration causes cationic deficiencies of two types--primary and secondary. The primary deficiencies are the result of residual solutions associated with pegmatites, carbonatites or deuteritic rocks. Pseudomorphic substitutions are common and the exact type of replacement or alteration is dependent on the P-T-X nature of the residual solutions. A-site cationic deficiencies may be high (approximately 20 percent for members of the euxenite-polycrase and aeschynite-priorite series). The substitution of hydroxyls for oxygen reflects the formation from water rich residual solutions. At low temperatures the effect of the residual solutions is similar to the alteration by weathering. Again, there is leaching of A-site cations (secondary deficiencies), simultaneous substitution of hydroxyl groups for oxygen and an increase of absorbed water. B-site cations remain unchanged. In practice, the distinction between primary and secondary alteration is difficult because their results are very similar and their effects are often superimposed. Primary alteration is usually pseudomorphic and occurs during or immediately after crystallization and metamictization. Secondary alteration is a later effect that benefits from the metastability of the metamict state. Both of these effects may be obscured by later natural annealing or recrystallization of metamict material.

Compositional variations and changes in physical properties have been detailed by Ewing (8). Primary alteration (e.g., hydrothermal) causes a consistent increase in calcium content, generally a decrease in the uranium and thorium contents, a decrease in the absolute rare earth concentrations (the REE distributions usually remain constant), a slight decrease in B-site cations, and an increase in structural and absorbed water. Secondary alteration (e.g., weathering) is similar but produces

a decrease in calcium content, an increased leaching of A-site cations and relative increase in B-site cations. The refractive index, specific gravity and reflectance (546 nm) decrease with both types of alteration, but hardness (VHN_{50}) remains approximately constant in altered and unaltered areas of the same specimen. The deviation from stoichiometric proportions of A- and B-site cations with increased alteration results in complex recrystallization phase assemblages during annealing studies (500 to 1000°C at 1 bar).

In some cases alteration initiates recrystallization (9). The most striking features are spherulites (Fig. 1) which in thin section occur as pale-yellow metamict polycrase. Under crossed nicols the spherulites exhibit a moderate birefringence which increases in the center region. The surrounding polycrase is metamict and isotropic. The individual fibrils of the spherulites are less than one micron in diameter and seldom distinct. In rare cases the extinction uniaxial isogyre characteristic of spherulites is observed. The spherulites occur throughout the specimen but are generally more concentrated along the numerous microfractures, where they coalesce forming alteration zones parallel to the microfractures. Compositional variations are summarized in Table 1.

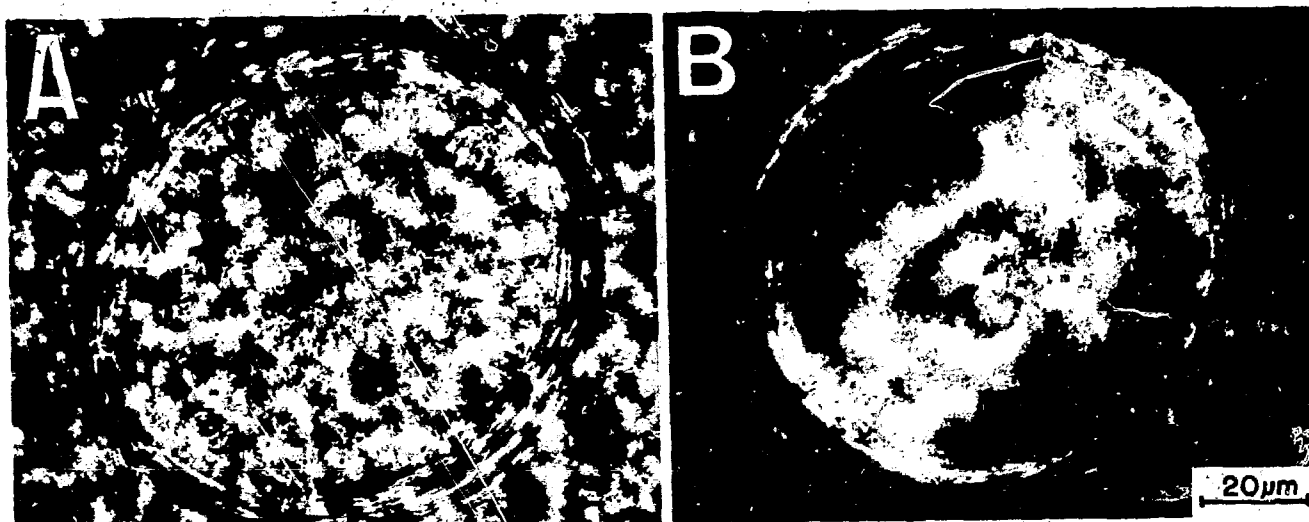


Figure 1. (A) Spherulite in transmitted light, individual fibrils barely distinct; (B) Spherulite under crossed Nicol prisms; the metamict matrix is isotropic.

Table 1

ELECTRON MICROPROBE ANALYSES IN TRAVERSE ACROSS SPHERULITE IN FIGURE 1

	TiO_2	Nb_2O_5	Ta_2O_5	CaO	$\text{U}_3\text{O}_8^{\text{a}}$	ThO_2	$\text{Fe}_2\text{O}_3^{\text{a}}$	$\Sigma\text{Ce RE}^{\text{b}}$	$\Sigma\text{Y RE}^{\text{c}}$
outside of spherulite	36.60	13.76	4.15	0.27	3.40	7.40	0.75	3.25	22.24
edge of spherulite	35.21	13.14	3.85	1.88	3.10	7.00	0.67	3.13	21.06
center of spherulite	35.82	12.92	4.05	1.87	3.20	7.35	0.75	3.19	21.91
edge of spherulite	37.02	13.71	4.00	1.86	3.15	7.10	0.76	3.20	21.54
outside of spherulite	37.27	13.57	4.15	0.31	3.50	7.75	0.71	3.27	22.17

(a) Analyzed as U_3O_8 and Fe_2O_3 on microprobe; therefore oxidation state not determined.

(b) $\Sigma\text{Ce RE} = \text{Ce}_2\text{O}_3 + \text{Nd}_2\text{O}_3 + \text{Sm}_2\text{O}_3$

(c) $\Sigma\text{Y RE} = \text{Y}_2\text{O}_3 + \text{Gd}_2\text{O}_3 + \text{Dy}_2\text{O}_3 + \text{Er}_2\text{O}_3 + \text{Yb}_2\text{O}_3$

RADIATION DAMAGE EFFECTS

Thorite and huttonite are the two known stable phases of ThSiO_4 . Both phases occur naturally, but show markedly different behavior toward metamictization. Thorite is often found as euhedral tetragonal grains which are partially or fully metamict while huttonite has been found only in the crystalline state. Thorite is isostructural with zircon, also often found in the metamict state; and huttonite is isostructural with monazite, found only in the crystalline state. Since thorite and huttonite are isochemical, they receive about the same radiation flux and provide models for examination of structural controls on radiation damage. Structure refinements of both phases have been completed in order to place further discussion of the behavior of these two phases toward metamictization on a firm structural basis (10).

Huttonite is monoclinic, space group $P2_1/n$, with $a = 6.784$, $b = 6.974$, $c = 6.3188 \text{ \AA}$, $\beta = 104.92^\circ$, and $Z = 4$. The huttonite structure consists of a three-dimensional network of edge-sharing thorium polyhedra which are interconnected by SiO_4 tetrahedral monomers. Each thorium atom is coordinated by four axial oxygens and five equatorial oxygens, for a total coordination number of nine. The axial oxygens are connected to silicon atoms forming Si-O-Th-O-Si linkages. The equatorial oxygens form a nearly planar pentagonal array around thorium in the plane perpendicular to the axial direction.

Thorite is tetragonal, space group $I4_1/amd$, with $a = b = 7.1328$, $c = 6.3188 \text{ \AA}$, and $Z = 4$. In thorite, the thorium atom is coordinated by four axial and four equatorial oxygens for a total coordination of eight. The axial oxygens are bonded to thorium and silicon such that SiO_4 shares opposite edges with the ThO_8 group forming chains parallel to c , identical to those in huttonite. Both the axial and equatorial Th-O distances in thorite are about $0.1 \text{ \AA}$ shorter than their counterparts in the huttonite structure.

The mechanism for conversion of a crystal to the metamict state is not fully understood, though it is believed that destruction of the crystal lattice by recoiling daughter nuclides of fission events is important. The principal structural difference between thorite and huttonite is the large void space present in thorite. The voids are centered on fractional coordinates (1/4, 1/2, 1/2) with an approximately octahedral shape and a volume of $14.0 \text{ \AA}^3$. They are interconnected to form channels parallel to c and could be responsible for the diffusion of water into the thorite structure. In view of the fact that natural thorites may contain up to 70 mole percent water (11), hydration may play a major role in the metamictization process. Roy (12) has postulated that the process of metamictization requires structures with voids large enough to accommodate displaced ions. Additional experiments examining the role of water and the detailed nature of the metamict state are in progress.

SUMMARY

The efficacy of studying alteration and radiation damage effects in metamict minerals is that they provide models for the evaluation of long term effects that cannot be reproduced in the laboratory. Other natural analogues such as volcanic glasses and tektites may provide information on the long range stability of glasses as a function of pressure, temperature and composition (e.g., most volcanic glasses for which age dates are available are less than 2 m.y. old). Effects of radiation damage (e.g., fission tracks) on the same types of glasses may provide information on such factors as: (1) self-induced annealing (fission track fading) as a function of temperature and composition, and (2) increased susceptibility to leaching as a result of radiation damage along track paths.

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RADIATION DAMAGE IN CERAMICS*

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Radiation damage of ceramics, while having some resemblance to the more-frequently studied damage effects in metals, has two characteristics which make it unique: The presence of two sublattices, and the electrically-insulating nature of most ceramics. These characteristics can significantly affect mechanisms of damage, nature of damage formed, and physical properties relevant to nuclear waste disposal.

DAMAGE MECHANISMS

Structural damage to ceramics can be induced either by ionizing radiation or by particle bombardment. With respect to the former, the creation of electron-hole pairs by bulk electromagnetic radiation causes atomic displacements in some insulators when energy of the exciton is released nonradiatively during recombination. This mechanism, first described by Pooley (1) and Hersh (2) is effective only in ceramics whose minimum displacement energy is relatively low, and then apparently only on the anion sublattice. The effect is primarily observed in alkali halides, and has not been reported in refractory ceramics.

Damage by the Pooley-Hersh mechanism can also occur with particle bombardment, since a portion of the energy deposited is dissipated in electronic excitation. Again, however, energy available to form Frenkel pairs is limited to that released by electron-hole recombination, since the lifetime of highly-energetic electronic excitation before its decay to the excitonic state is probably too short to cause displacements (3).

* Work performed under the auspices of the U.S.E.R.D.A.

A second type of ionization-induced damage may occur as a result of particle irradiation. Here the damage is manifested as tracks of disturbed material, the characteristics of which cannot be satisfactorily explained by collision effects alone. A useful, though not proven, explanation is based on displacements resulting from mutual electrostatic repulsion of positive ions in a zone heavily ionized locally by a passing particle (4,5). Tracks are usually the result of spontaneous fission of actinides, where damage is by heavy energetic particles capable of inducing a high rate of primary ionization. However, there is evidence that lower ionization rates can also cause track formation (6).

Even when ionizing radiation is unable to create displacements in ceramics, physical properties can be affected by such irradiation. This is because some defect parameters such as minimum displacement energy or mobility can be a function of charge state, which can be altered by ionizing irradiation. Thus the ratio of ionizing to displacive energy must be considered in a complete description of the damage environment.

Particle bombardment-induced displacements occur in ceramics in much the same way as for metals (i.e., by direct knock-ons). An important distinction is that minimum displacement energies and cross-sections may differ for the two ceramic sublattices, so that the numbers of anion and cation Frenkel pairs formed may be different. This can have a profound effect on the nature of stable defect aggregates formed.

NATURE OF DISPLACEMENT DAMAGE

Bulk ionizing radiation can produce only isolated Frenkel pairs in susceptible materials, because of the low energies available from each exciton decay. With particle irradiation, the particle itself or primary knock-on atoms can have high velocities and may deposit significant amounts of energy over their range by electronic excitation and creation of further displacements. The large amounts of energy deposited can lead to formation of displacement spikes (microvolumes containing high densities of

displacement damage). In ceramics the result can be localized mixing of anions and cations; if subsequent cooling of the spike is on the order of the period of atomic vibration, as appears likely (7), the severely-disordered structure can be quenched in and stable damage aggregates formed.

Thermal spikes (microvolumes where intense energy deposition has temporarily increased lattice vibrations) may also be formed. These could be important to damage processes if they are overlapped in time and space by displacive events. Near-surface thermal spikes can also increase vaporization rate (8).

Displacement cascades (the totality of displacement events initiated by an energetic particle) could, if they overlap, create new forms of damage. However, calculations show that this is unlikely even at very high damage rates (7).

Point defects in ceramics can aggregate to form point defect complexes (e.g., divacancies), dislocation loops, or clusters. In addition, larger three-dimensional agglomerates may be formed. Several investigators have identified such defects in photon-irradiated alkali halides as cation collids. Hobbs and Hughes found both colloids and what are apparently anion inclusions (9). They postulated that the former resulted from anion vacancy aggregation, and the latter, from precipitation of anion molecular defects. On the other hand, preliminary results by Bunch and Hoffman suggest that aggregates in neutron-irradiated Al_2O_3 are pores (10). These could result from precipitation of a stoichiometric ratio of aluminum and oxygen vacancies. At present it is not possible to predict which type of three-dimensional aggregate will form in a particular ceramic; however, such defects must be identified before their effect on physical properties can be understood.

Some crystalline ceramics are thermodynamically near the glassy state, so it is not surprising that radiation-induced disordering of the lattice can result in the formation of amorphous structures. This apparently occurs by overlapping of damage zones (11). Naguib and Kelly (12) correlated the likelihood of such a transformation with crystallization temperature and degree of ionicity. It was predicted that

amorphization should occur when the first factor exceeds $0.30T_m$ or when the second is less than 0.47.

Naguib and Kelly also studied the likelihood of stoichiometry changes under irradiation. It was concluded that such changes could result at high damage levels if a minimum occurs in the heat of atomization at a particular degree of loss of a component.

The nature of permanent damage formed in ceramics may be a function of relative rates of damage and annealing processes. Such an effect has been found in high-damage-rate studies of metals, where irradiation temperatures must be adjusted upward to simulate damage effects found at lower rates (13). The wide variation in damage rate with time for solid nuclear waste, and the necessity for accelerated laboratory testing, indicate that rate effects must be carefully considered.

EFFECT OF RADIATION DAMAGE ON PHYSICAL PROPERTIES

One of the major irradiation effects in materials is swelling. Ceramics can exhibit growth either as a result of an accumulation of point defects or because of defect aggregation. The latter effect, which is an elevated-temperature phenomenon, is the more significant. Here creation of new lattice sites is primarily responsible for growth.

The most familiar example of ceramic swelling is that of fission reactor fuels such as UO_2 . In these materials, vacancies resulting from fission-induced displacement damage combine with fission gases (Kr, Xe) to form stable bubbles. The volume of the bubbles, which is equivalent to the volume of new lattice sites created, can approach 10% (14). Non-nuclear ceramics are also subject to swelling; Al_2O_3 irradiated to ~ 3 displacements per atom (DPA) with neutrons at elevated temperatures expands several volume percent (15). In this material the process responsible appears to be pore formation (10).

Some ceramics exhibit near-zero dimensional changes at temperatures and damage levels where others swell significantly (16). This may be due either to intrinsically

low-swelling modes of defect behavior, or to different temperature dependences of swelling. Neutron-irradiated ZrO_2 shows little density change at 650 and 1025 K, but swells ~2 vol.% at 875 K; these temperatures correspond to 0.22, 0.29, and 0.34 T_m (17). By contrast, Al_2O_3 shows increased swelling with temperature at the same temperatures (0.28, 0.38, and 0.44 T_m for this compound) (15).

If irradiation-induced defects aggregate or anneal suddenly rather than gradually, the stored energy released will cause a temperature rise of the matrix. Such a release would usually be triggered by heating. Since the thermal energy of the solid waste will decrease with time, the only way that a rise in temperature might occur is through a reduction in thermal conductance of the system. This could result from structural changes or cracking in the ceramic. Even with adiabatic heating, temperature rises are not expected to be large (18). Nevertheless, the likelihood of sudden stored energy release, its magnitude, and its effect on the solid waste should be considered for each candidate material.

Mechanical properties of ceramics at low temperatures generally change under moderate irradiation in the direction of increased hardness and strength. There is also some evidence of decreased microscopic plasticity (19). These effects can be explained by postulating a reduction in dislocation or crack mobility resulting from the presence of radiation-induced debris. Details of mechanical behavior will depend on the nature of the defect structures formed in each ceramic.

At high dose levels, anisotropic grain growth in polycrystalline non-cubic ceramics such as BeO can cause microcracking and drastic reductions in strength (20). Another mode of structural failure in materials containing large quantities of insoluble gases is bubble formation. In elevated-temperature tests of PuO_2 , helium from alpha decay is found to form bubbles along grain boundaries (21) this could also lead to significant loss of strength.

The role of gases in swelling and mechanical property degradation must be considered for nuclear waste ceramics, where helium is also generated by alpha decay.

The following table gives estimated concentrations of this usually-insoluble gas for low- and high- activity solid wastes* as a function of time of storage:

HELIUM CONTENT OF WASTE

<u>Storage Time</u>	<u>Low Activity</u>	<u>High Activity</u>
1 _{yr}	10 appm	100 appm
10 ² -10 ³ yrs	100 appm	1000 appm
10 ⁵ -10 ⁶ yrs	1000 appm	1 at. %

These quantities of gas can be significant in aiding void nucleation (at lower concentrations) or forming significant volumes of equilibrium bubbles (at the higher levels).

Elevated-temperature creep can be significantly enhanced by irradiation. In UO₂, creep at temperatures below ~1500 K is greater in-reactor than out, and below 500 K is athermal (22). The explanation proposed for these effects is that interstitials created by radiation damage migrate to dislocations and enhance their mobility. In polycrystalline materials subject to anisotropic grain growth, internal strains can also contribute to creep enhancement.

A post-irradiation decrease in creep rate of metals below that characteristic of the unirradiated material has been observed (23) here, radiation-induced defects impede dislocation motion. Since damage rates in nuclear waste ceramics will decrease greatly with time, such irradiation hardening at elevated temperatures could result.

Thermal conductivity of insulators is reduced by both point and aggregated defects, since each scatters the phonons by which heat energy is transmitted. Neutron irradiation of Al₂O₃ at ~1000 K to ~1-10 DPA results in a reduction of thermal conductivity at that temperature by roughly a factor of two; the fractional reduction is greater at 323 K (24). A tendency toward saturation is observed at higher doses.

* Low-activity wastes are those derived from UO₂ fuel; high-activity wastes result from the use of mixed-oxide fuel. Activities are given in ref. 18.

Calculations of the contribution from both point and extended defects show that at these temperatures the former are nearly twice as effective in reducing conductivity as are the latter, for a fixed number of defect sites (24).

Irradiation-induced defects can affect diffusion rates both of component species and of gases. A higher-than-normal concentration of point defects should enhance self-diffusion, and therefore accelerate such diffusion-dependent effects as phase transformations. Migration of gas atoms is affected in complex ways by radiation damage, with either enhancement or retardation possible (26,27) kinetics of bubble formation might thus be altered.

Since annealing of radiation damage increases sharply with temperature, very-high-temperature phenomena such as vaporization should not be greatly affected by prior damage. (Unless, of course phase changes have occurred.) However, concurrent thermal spike formation can enhance vaporization rate (8). Leachability, a low-temperature phenomenon, may on the other hand be affected by the presence of radiation-induced defects. The preferential etching of fission tracks shows that damaged microvolumes can be chemically less stable than is the matrix. Locally-enhanced leach rates could have deleterious effects even if bulk rates are not increased. One example is the possibility that fission products might have preferentially segregated into high-leach-rate zones. Another is the possible formation of localized surface irregularities at which premature fracture might be initiated.

Radiation damage can lead to major structural changes in the matrix of some ceramics. If irradiation induces a significant stoichiometric shift, (e.g., from MoO_3 to MoO_2), virtually all physical properties will be altered. However, such an effect occurs only in selected ceramics and at damage levels on the order of 10-100 DPA* (28). Roughly 10^{20} - 10^{21} alpha decays/g of nuclear waste would be required

* These and the following DPA values were calculated by use of the Kinchin-Pease relationship (29), neglecting alpha-particle damage, and should be considered only rough estimates.

to generate this damage level (primarily through recoil effects); since such doses are not expected even after a storage life of 10^6 yrs (18), a stoichiometric shift does not seem likely.

Amorphization can take place at a wide range of damage levels, depending on the material. Metamictization (conversion of some minerals from crystalline to amorphous forms by natural radioactive decay) requires $\sim 10^2$ - 10^5 years, depending on activity level (18). Thus amorphization with consequent major changes in physical properties is possible in ceramic nuclear waste. However, not all ceramics are susceptible to this structural alteration, so that the potential problem may well be avoidable by proper selection of the waste form used.

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NOTES ON RADIATION EFFECTS IN GLASSES PERTINENT TO SOLID
STORAGE OF RADIOACTIVE WASTES

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INTRODUCTION

The behavior of silicates and oxides containing dispersed radioactivity has been under investigation for a long time. Berzelius described the pyrogonomic property of gadolinite (2), a phenomenon he learned about from Wollaston. By the 1890's a number of minerals were known which had the external form of anisotropic crystals, but which did not exhibit a corresponding anisotropy in their optical properties. These were termed metamict. Geologists and mineralogists through the 1940's were uncertain of their origin; radioactivity, leaching, and replacement were hypotheses. Following Seitz' presentation (3) of his work on radiation effects during World War II, Pellas (4) related this work to the problem of the metamict state. Today we are certain that this state is caused by radiation damage by the naturally occurring radioactive content. This behavior is therefore pertinent to the subject of this workshop. The first important point about the process was made by Holland (5): in the metamictization of zircon he considered that the effect of the beta and gamma rays was negligible and that the recoil decaying nucleus was 20 times as effective as the emitted alpha particle. The second important point is that a material which normally does not accumulate radiation damage when the irradiation is external may do so with dispersed radioactivity; such has been reported for alumina dispersed in fissionable material placed into a nuclear reactor (6) and for zirconia containing heavy elements (7).

Severe changes in vessels used to contain radioactive solutions was noted by the early investigators of radioactivity (8). There were reports of embrittlement and cracking. We attributed these effects originally to dimensional changes caused by alpha bombardment. We now know that ionization can be an effective agent in the case of glasses (9) and that chemical effects are involved also (10). The problem of storage of radioactive solutions has been investigated and specifications for glasses which are stable for this purpose have been made (11,12).

Further sources of information are the behavior of materials in radiation environments; e.g., reactors, accelerators, or cells used for the storage or handling of radioactive materials. Three reviews written in the mid-60's stress different aspects of the radiation effects (9,13,14). Another source of pertinent information is the studies of charged particle tracks (15,16,17). The last general literature search was concluded about 1960 (18). A more specific search made in 1965 was directed toward vitreous silica but included many items on other glasses and on quartz (9). Most of these items relate to properties of glasses. Most of the radiation effects items deal with the problem of coloration in glass, for the problems of cave windows and optics were being studied in that period. However there were several items which dealt specifically with storage of radioactivity; in particular, a Monaco conference in 1959 (19), an IAEA symposium in Vienna in 1962 (20) and a few individual studies. None of this material has been examined critically. A compilation of pertinent references has been provided which has been supplemented periodically (21).

There have been frequent conferences on the management of radioactive wastes. Most of the material presented at these conferences has dealt with various proposals and examples of storage and with the technology of transforming the wastes into a particular form. There are several exceptions. Heimerl, et al. (22), were concerned with the stability of the glass toward devitrification and toward leaching, but how

the behavior might be affected by the radioactive content of the glass was not considered.

Grover (23) studied the effects of temperature, of irradiation with thermal neutrons causing ^{10}B fissioning, and of gamma irradiation in spent fuel elements. He concluded that the effect of temperature on leaching was greater than that of radiation, but that radiation enhanced the temperature effect, particularly in the case of phosphate glasses. He found borosilicate glass preferable to a phosphate glass for the fixation of high level wastes. Watson, Aikin, and Bancroft (24) considered the leaching problem, but did not consider the effect of radiation on the glass or on leaching. A symposium at a recent meeting of the American Ceramic Society (25) dealt with investigations in progress at several laboratories. Mendel has outlined an extensive program plan for characterizing solidified high-level wastes (26), and some results from this program are beginning to appear (27) and are presented earlier in this report.

Most of the content of this paper arises from specific investigations of glasses and allied materials which were performed at ANL, which were directed toward other ends, but which are pertinent to the purposes of this workshop. These were studies of radiation effects which occur in oxides and silicate glasses and relate to changes in internal stress, diffusion, and leaching which may occur on long term storage; and to the problem of permeability of the materials to gases.

DILATATION AND INTERNAL STRESS

Dilatation (i.e., fractional or percent volume changes) of glasses caused by radiation may be either positive or negative. Various causes of dilatation may be operating simultaneously. The effects appear to be additive. They may have different rates and saturations causing the net dilatation to alter in complex ways and even change sign during the course of irradiation (28). Among the causes of

dilatation in oxides and silicate structures, the following have been identified positively:

1. **Compaction:** The oxygen in most silicate structures is not symmetrically bonded to silicon. Thus, any source of thermal or vibrational excitation, and even the static process of compression, causes a small alteration of atomic configuration. In a disordered structure (e.g., the glasses) the structural change is not rapidly reversible and is easily quenched in, resulting in a compaction. Compaction can be released by thermal annealing and by other processes, such as by ionizing radiation, which cause cleavage of the Si-O network. Compaction by irradiation appears to contribute, at maxima, about negative several percent to the dilatation (29,9).
2. **Network cleavage centers:** Starodubtsev and Azizov (30) reported a positive dilatation of about 0.02% for a sample of vitreous silica subjected to gamma irradiation. The effect was ascribed to cleavage of the Al-O-Si bonding by Primak and Kampwirth (28).
3. **Thermal quenching of expansion:** In vitreous silica, quenching of the heated vitreous silica causes a compaction. The reverse effect, an expansion occurs for many glasses (31). It is attributed to movement of the non-network ions. The effect is small. This writer is unfamiliar with any radiation effects associated with this process.
4. **Color center formation:** Trapping of electrons in vacancies can cause an expansion. This effect is best known for the alkali halides (32). It has also been found for magnesium oxide (33). It may therefore be anticipated in glasses, particularly those loaded with oxide additions, as would be the case for solid waste bodies. Paymal has reported a positive dilatation in excess of 1% for a boron-containing flint glass subjected to neutron irradiation (29).

5. Gas swelling: Gas trapping, such as that of the helium formed in radioactive decay, by lithium or boron fissioning in a nuclear reactor, or by ion implantation can cause large dilatations. The case of ion implantation has received the most study (34). Paymal described the behavior of neutron irradiated boron-containing glasses (29). In ion-implantation, surface disintegration is usually seen by 7 atomic percent of injected gas. Typical dilatations are about 0.8% for 10^{20} gas atoms/cm³. It is estimated that retention of all the helium gas formed during the radioactivity half-life of a glass loaded with 25 wt% of a heavy element would cause 2/3% dilatation.
6. Post-irradiation heating of glass containing trapped gas: Paymal found increases in dimensions for a neutron irradiated magnesia-alumina containing borosilicate glass when it was heated to temperatures near the softening point, and the samples became greatly deformed (29). The section of his thesis describing these results is reproduced in the Appendix to this paper, and the most pertinent section is translated.

If the waste glass material were homogeneous, the dilational effects caused by beta and alpha waste glass particles and heavy element recoils would be uniform. The effects of gamma rays would not be (35). More serious would be the effects of temperature, because the bodies will be subjected to heating by their radioactive content. The attendant thermal gradients may cause gradients of as much as a percent variation of dilatation through the body. Because the moduli are so large, the forces are large, but because of the small volume change, the energy stored is small, estimated at less than 0.1 cal/g, less than the amount required to raise the temperature of the body 1/2°C; there is certainly no danger of an explosive reaction. The danger is limited to stress concentration, mechanical cracking by crack propagation. The energy stored in gas retention through a half-life would be about 0.028 cal/g, equivalent to about 1/7°C temperature rise. It would seem that

mechanical arrangements or containers capable of withstanding 2% dilatations in their contents should provide containment adequate for radiation associated dilatations. Some peculiar effects like frothing or expulsion may occur when heating containers long in storage.

LEACHING

Leaching is usually tested independently of radiation behavior. Unfortunately, radiation may have a profound effect on the leaching stability of glasses. The mobility of the alkali on ion bombardment is well known (13). It is less well known that alkali mobility is retained, post-irradiation (10), to the extent that the alkali will migrate to the surface forming material deliquescent at typical relative humidities. It is reasonable to assume that this material would be subject to leaching. Glasses normally considered chemically durable seem not to show the post-irradiation alkali migration effect, but yet exhibit alkali migration on irradiation. A probable mechanism for the alkali migration is reduction of the valency of a heavy element freeing an electron for neutralizing the alkali ion. The alkali atom appears to be mobile in the glass matrix. The effect should therefore be enhanced by incorporation of heavy elements in the glass. The effect is particularly noticeable for the alkalis, lithium and sodium. Heimerl, et al. (22), found that (in the absence of radiation) sodium was leached faster than cesium, but that after devitrification cesium was leached faster than sodium.

Presumably, migration can take place only to a free surface, hence, it should be most serious in pelletized glass, glass sheets, or contained glass which had fractured. The effect of the alkali on containers must be considered and also the effect of the loss of alkali from the glass. The loss of alkali would affect the permeability to gases and may affect the retention of other constituents. Loss of alkali may also enhance devitrification.

Other evidence for a change in leaching characteristics on irradiation is found in studies of ion tracks in glass (15). In this work, the tracks are developed with weak etchant solutions. Since the etching rate of silica increases by orders of magnitude in the series stishovite, coesite, quartz, vitreous silica, the density and integrity of the Si-O network must be a factor. Since radiation cleaves the network, this may be part of the explanation for the greater solubility of the tracks. However, the exact mechanism (16) does not appear to be known, and should be investigated further.

In a recent investigation performed in this laboratory (to be published), optical behavior indicated that a glass may lose its non-silica content under bombardment at room temperature with light gas ions (protons, deuterons, or He^+). ranges about $1\ \mu\text{m}$ without undergoing collapse of the Si-O network. Other effects, not yet understood, occur in the temperature range up to a few hundred degrees above room temperature; they may indicate gross diffusion.

GAS RETENTION

Vitreous silica and Pyrex appear to be permeable to helium, hydrogen, and deuterium implanted in thin layers. When non-network ions are introduced into the glass, gas permeability is reduced (34). Thus, crown glass and borosilicate crowns are permeable to helium but are not permeable to hydrogen or deuterium. The dense barium crowns are permeable to neither hydrogen nor helium. A special glass which would be in the class of a magnesia-alumina-borosilicate crown has also been reported to trap helium formed in neutron irradiation (14,29). In the thin layers studied in ion bombardment, the gas appears to cause the development of a micro-porosity with attendant swelling. The pores then grow by coalescence. In most materials this occurs at a definite depth, and it appears to be influenced by the stresses developed in the body by the dilatations attending ion bombardment. In

one of the glasses bombarded with protons, the crown glass C-1, a more general frothiness appeared to develop. Dense barium crown appeared to be more brittle to this treatment, and the destruction of the surface occurred at much lower dose than for other materials; very large effects were seen by the implantation of only 2.25 atom% of helium. However, this glass must have contained over 40% baria, a larger proportion of heavy oxide than is planned in radioactivity storage. Since the total decay of a heavy element would introduce about 2.7 atom% of helium, it would be desirable to determine the behavior of the particular body or glass to such entrapment even though it is probable that bodies in which the gas is homogeneously distributed would be much more stable than the thin layers formed in ion bombardment, and most of the wastes would have sufficiently long radioactivity half-lives that no present danger would be involved.

Gould and McDonnell (36) reported radiation blistering effects in materials in contact with ^{252}Cf .

Our studies of the thermal behavior of implanted gas have just begun. Post-implantation heating behavior and high temperature bombardment behavior differ. Retention is decreased by even moderate increases in ion-bombardment temperature. When retention occurs at high temperature, surface destruction is seen at smaller dose presumably because of the high gas pressure and because of the reduced moduli of the material. Pyrex glass showed a shrinkage when bombarded at elevated temperature but nil dilatation at room temperature. This study is continuing. Reports of studies of the heavier rare gases indicate a higher retention for these than for helium (13,37). However, older work on the release of radon from rocks would indicate that special studies may be required for bodies suitable for its containment. Problems of containment for volatile oxides have been considered (38).

GLASS FUEL ELEMENTS

Glass fibers were studied by Harteck, Dondes, and Lockwood (39). Over 200 glass compositions were prepared by them. These would be classed as heavy metal oxide crown glasses, mostly in the light category (e.g., LUC, light uranium crown). During irradiation with thermal neutrons they report that the only radioactive isotopes found in a coolant gas stream were xenon, krypton, bromine, and iodine and that more than 99% of the nonvolatile fission products were retained in glass wool and other filtering media which had been placed in the gas line. No aerosol of fission products was formed. No fragmentation of the glass fibers was noted even where over 90% of the fission fragments left the glass (small diameter fibers). This effect was considered to represent a "self annealing" property of the glass fibers. It should be noted that the irradiation caused a considerable rise in temperature and that some of the fibers melted. One great advantage claimed for these fibers, at least as prepared, was containment, LPuC (light plutonium crown) glass "wiped clean"; no alpha activity was detected.

Massive samples of uranium-containing silica glass and boron-containing silica glass were irradiated in the MTR by Cashin and Howland (40). Temperatures reached were in excess of 600°C. Fission gas release was negligible, but practically all of the helium was released. Surface cracking was severe and was attributed to swelling. They concluded that because of the cracking of the glass, in service it must be held by a structural material which need not be a pressure vessel.

Lungu, Ribco, and Beleuta (41) irradiated silica-uranium glass-ceramics, with 40, 50, and 60 mol% UO_2 . Only contraction is reported, saturating at 1%, but at the 40% and 50 compositions, an initial contraction of 2% was found (supervenant expansion (9)).

INTERNAL HEATING, SEGREGATION, DEVITRIFICATION, CRYSTALLIZATION

Crystallization of specimen waste storage glasses as a function of temperature was studied by Heimerl, et al. (22). They identified phases which precipitated and how leaching characteristics were affected. These matters are beyond the scope of this paper which deals with radiation effects.

Data for the radiation behavior of materials has been accumulated mainly for small homogeneous bodies irradiated near room temperature. Particularly for oxides, silicates, and ceramic bodies there is little information about their radiation behavior at elevated temperature. We can only speculate about the behavior of large canisters of such materials which are internally heated by their radioactive content and thereby develop a parabolic thermal gradient to the surface of the canister.

The effect of particulate radiation, hence of the alpha particles and heavy element recoils, at room temperature is to homogenize the material and reduce it to an amorphous form: metamictization (42,43). However, when the amorphous forms developed in metamictization are heated in certain temperature regimes, segregation and crystallization can occur, as shown in Pabst's (43) investigations; and the slow rate of irradiation which would occur in most waste bodies might facilitate such a process. Thus, the devitrification of the glass might be enhanced; i.e., it might be observed at a lower temperature and occur in a shorter time because of the radiation. The result would be a non-uniform inhomogeneous body in which the constituents have segregated. The effect could be aggravated by thermal cycling in certain temperature regimes. No predictions can be made of the temperature regimes for such effects; experimental investigation of the particular composition of interest will have to be made.

When crystallization, segregation, or devitrification occurs, there is a radical change in the behavior of the body. Then each grain exhibits its own radiation behavior, the grains become highly stressed, and grain boundary effects are found. In several cases of inhomogeneous materials which were subjected to ion bombardment in this laboratory (44), the individual grains became highly birefringent, indicating high internal stress, grain boundaries become sharply defined, and selective radiation blistering was found on particular grains. Pits developing in the surface seemed to have formed by grain ejection.

There is some controversial evidence for crystallization of vitreous silica under irradiation in a nuclear reactor (8). Roy and Busmer studied the effect of nuclear exposure on phase changes in silica (45).

COMMENTS ON STORED ENERGY

Stored energy refers to exothermic reaction occurring during heating of a body. This is a severe problem in the case of carbon where irradiation causes the formation of relatively high concentrations of free carbon atoms which become mobile with relatively little heating and react to form C_2 with a large energy release. The problem is a severe one in the case of carbon because of its high Debye temperature and, hence, small heat capacity in this temperature regime. It is easy to obtain stored energy release in excess of the heat capacity leading to runaway temperature rises (catastrophic stored energy release)(46). Formation of such reactive species have not been found in the case of the oxides. Thus maximum heat releases expected are those involved in phase changes, under 50 cal/g; and with the higher heat capacities of these bodies, catastrophic effects are not anticipated. Usually, thermal effects of glassy bodies are spread over a large range of temperature; but in one study, in the thermal analysis of a neutron irradiated vitreous silica (grade unidentified), a surprisingly sharp peak was found at about 350°C. The stored energy was miniscule, however, some 2 orders of magnitude smaller than that

found for carbon (27).

GLASS CONSTITUENT CONTRIBUTION TO RADIATION BEHAVIOR

Silica: Shows compaction on irradiation except when network impurities are present. Network impurities may cause a rapid radiation expansion, presumably the result of network cleavage at the impurity site (28).

Borate: In a high silica glass there is a phase separation into a high silica phase and a high borate phase (47). These glasses show the high chemical durability of silica, but they have been reported to be unsatisfactory for containing radioactivity (48). They are specified for neutron absorbers, but for this application it has been found necessary that the short cylinders employed be highly tempered (49) (note that tempering and compaction cause a stress of the same sign). In addition, the radioactive waste solutions are loaded with fluoride ion which causes surface dissolution and only a 2-year lifetime is expected of these cylinders (49). Boron oxide glasses appear to hold compaction poorly (49). The high-silica glasses show the radiation compaction of vitreous silica (29). Borate in more complex glasses causes segregation on proper heat treatment and is used to prepare glasses with high leaching characteristics and special bodies starting from a glass melt (47).

Alkali: Alkali in glass will migrate on irradiation, and the migration may continue after irradiation (10). Alkali is the most diffusible normal constituent of a glass (51). Alkali reduces the permeability of the glass to gases. Molecular hydrogen is retained at room temperature, but not helium (34). The activation energy for diffusion, temperature range 300 to 600°C, in glass was reported to be less for cesium than for sodium (52).

Alkaline earth: Magnesia and baria in glass have been found to reduce permeability even to helium (34,14,29).

Alumina: Aluminum enters the Si-O network. The network appears to be sensitive to cleavage at the aluminum impurity; an extremely high efficiency for trapping of electrons produced in ionization has been inferred. The center and associated dilatation appear to anneal at quite low temperature, below 500°C (28).

Heavy elements: Those subject to valence change appear to be efficient hole traps. This is important, because the process can facilitate the migration of alkali and the formation of electron traps which cause dilatation. The heavy elements decrease the permeability of the glass to gases. The heavy elements introduce a positive component to the radiation-induced dilatation. They may embrittle the glass; i.e., reduce the rate of relaxation under stress, an effect which is facilitated by irradiation and by heating. They may cause very intense optical absorption on irradiation (53).

SUMMARY

The major problems which have been treated here have been development of internal stress and alterations in diffusion and migration of constituents of the glass or body on irradiation. The bad actor in glasses is the alkali content, but it is not known whether its migration will affect the migration or leaching of other constituents; it would be expected to have an effect on gas retention. The internal stress would have to be studied for the particular composition of interest because there are a number of dilatation effects which can occur simultaneously, and these are modified by the composition of the glass. The most serious matter is the lack of information about the radiation behavior of these materials as a function of the temperature of irradiation. It is imperative that more data for irradiation above room temperature be accumulated.

Studies of the effects of bombardment by protons, deuterons, and helium ions at various temperatures up to about the strain point of a variety of commercial glasses and up to about 600°C for various bodies are currently in progress in our laboratory. We are in a position to accept a limited number of samples for inclusion in this testing program. The material would have to be suitable for optical finishing (lapping and polishing) and be free from radioactive elements or other hazardous constituents (e.g., beryllia). The test samples currently in use are about 1/2 inch square or about 5/8 inch diameter and about 1/8 inch thick. Effects of ionization could also be tested.

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APPENDIX: From the doctoral thesis of André J. Paymal, l'Institut du Verre (Paris, 1962); also Paymal.²⁹

VI.3. — Verre ID.

La composition moléculaire de ce verre est la suivante : 56,10 SiO₂, 18,45 MgO, 9,00 Al₂O₃, 3,55 K₂O, 12,15 H₂O, et 0,75 Na₂O. Ce verre opalesce quand il séjourne un certain temps à une température de l'ordre de 700 °C à 900 °C. Cette opalescence s'accompagne d'une augmentation de densité de l'ordre de 90.10⁻⁴ g.cm⁻³ (pour un traitement de 30 mn à 800 °C), d'une augmentation du module d'élasticité de l'ordre de 1 %, et d'une diminution importante du coefficient de dilatation qui passe de 50.10⁻⁷ °C⁻¹ à 5.10⁻⁷ °C⁻¹ environ. Nous avons pensé que l'irradiation pouvait être susceptible de faire dévitrifier ce verre.

Irradié dans des flux inférieurs à 10¹⁸ n.cm⁻².s⁻¹, le verre ID subit un effet de compaction important qui se traduit par une augmentation de densité de 400.10⁻⁴ g.cm⁻³ environ pour des doses comprises entre 1 et 2.10¹⁸ n.cm⁻². Irradié dans des flux supérieurs à 10¹⁸ n.cm⁻².s⁻¹ ce verre présente une augmentation moindre de sa densité; ce résultat est similaire à celui du Pyrex et semble commun à tous les verres qui subissent l'effet de compaction. Le nombre des irradiations effectuées est trop faible pour que l'on puisse tracer une courbe de variations de propriétés en fonction de la dose; nous avons seulement indiqué sur la figure 40 trois points P, Q et R qui correspondent respectivement

aux doses de 9,64, 21,4 et 57,4.10¹⁸ n.cm⁻² et indiquent les variations correspondantes de densité, module d'élasticité et résistivité électrique. Les variations de densité rappellent celles du Pyrex, celles de module sont différentes, sans doute parce que le verre ID est beaucoup plus sensible à la trempe que le verre Pyrex; l'écart de résistivité entre les échantillons Q et R

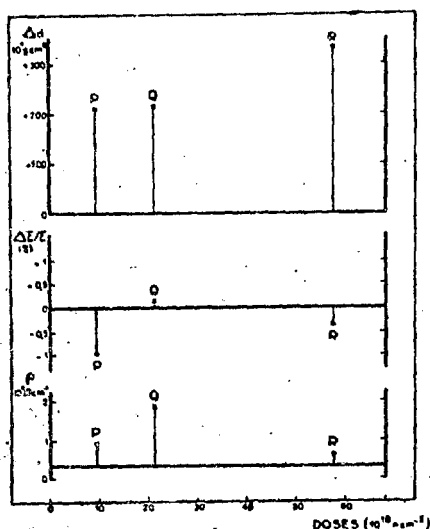


FIG. 40. — Variations de poids spécifique, module d'élasticité et résistivité électrique de trois échantillons de verre ID, P, Q et R irradiés respectivement aux doses de 9,64, 21,4 et 57,4.10¹⁸ n.cm⁻².

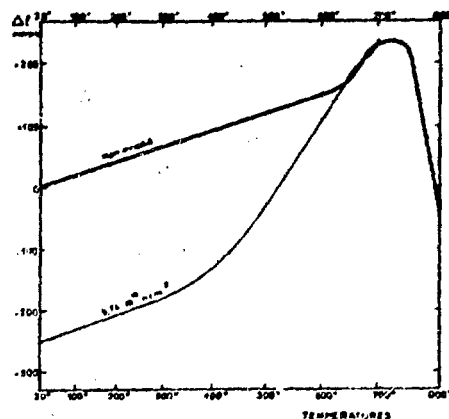


FIG. 41. — Allongement en fonction de la température de guérison du barreau R du verre ID.

pourrait peut-être s'expliquer par la présence du lithium de transmutation qui participerait à la conductibilité électrique; un dosage chimique sur l'échantillon R a révélé la présence de 0,3 % environ de lithine. La courbe de guérison (fig. 41) de l'échantillon R semble infirmer la possibilité de dévitrification de ce verre aux doses utilisées, car la guérison paraît totale au point de recuisson et le coefficient de dilatation du verre irradié est pratiquement inchangé. Par contre, la présence d'hélium se manifeste de façon spectaculaire par un gonflement du verre qui apparaît entre 600 °C et 700 °C et se poursuit très rapidement au-delà de 700 °C, d'autant plus violemment que le verre est plus irradié. On l'a vérifié par des mesures de densité sur de petits échantillons traités une demi-heure à chacune des températures indiquées sur la figure 42. Sensiblement

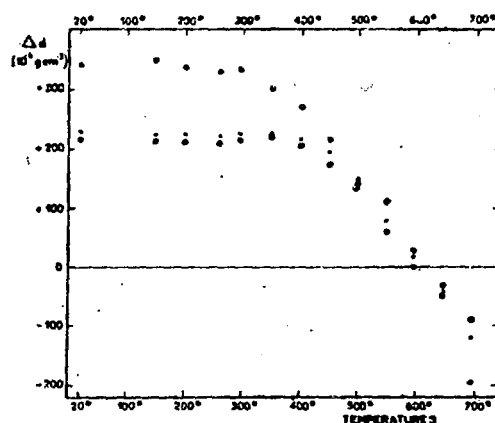


FIG. 42. — Variations du poids spécifique à 20 °C de petits morceaux de verre ID correspondant à des traitements thermiques répétés (séjours de 30 mn à chaque température indiquée). On remarquera que, au-delà de 600 °C, le poids spécifique diminue au-dessous de sa valeur d'origine. Ce fait est attribué à la formation de bulles d'hélium pendant le séjour à des températures du domaine de ramollissement du verre.

Doses : ● 57,4.10¹⁸ n.cm⁻²;
+ 21,4.10¹⁸ n.cm⁻²;
○ 9,6.10¹⁸ n.cm⁻².

en même temps que le gonflement on peut observer à l'œil des traces d'opacification à des températures plus basses que pour des échantillons non irradiés. Cette tendance à la dévitrification plus forte peut s'expliquer dans les verres irradiés par la présence de lithium, par leur structure perturbée ou peut-être par une certaine nucléation (130). Les amorce de dévitrification peuvent aussi constituer des points favorables à l'apparition des bulles et le gaz se manifeste par un gonflement homogène dans toute la masse, les dimensions des échantillons se trouvent dilatées, et c'est ainsi que le barreau R s'est allongé de près d'un tiers de sa longueur (fig. 43).



FIG. 43. — Déformation de barreaux de verre 1D au cours de la guérison, après que l'allongement eut atteint l'amplitude maximale du dilatomètre (à gauche, le barreau témoin).

VI.4. — Conclusion concernant les verres irradiés à hauts flux et à doses élevées.

Les quelques résultats exposés dans ce chapitre correspondent à une densité de réactions de plus de 10^{10} cm^{-2} ; ils nous permettent de constater que les produits de la fission du bore ont une action directe sensible sur les propriétés des verres. Il est possible aussi, pour des doses de neutrons thermiques très grandes, que les produits d'autres réactions nucléaires puissent intervenir. En tout cas l'échauffement des échantillons exposés à des flux importants, surtout pour les verres à fortes teneurs en bore, est susceptible de provoquer des modifications des propriétés très différentes de celles obtenues à des flux suffisamment faibles pour ne pas échauffer sensiblement les échantillons.

Translation of last part of p. 48 of the Thesis of A. J. Paymal (1962) about the behavior of an irradiated magnesia-alumina containing borosilicate glass on heating:

... On the contrary, the presence of helium is manifested in a spectacular manner by a swelling of the glass which appears between 600°C and 700°C and takes place very rapidly beyond 700°C; all the more violently the more the glass is irradiated. This was verified by measurements of density on small samples heated a half hour at each of the temperatures indicated on Fig. 42. One can also observe visually traces of opacification at lower temperatures than for unirradiated samples. The greater tendency toward devitrification in the irradiated glasses can be explained by the presence of lithium, by their perturbed structure, or possibly by the beginning of nucleation.¹³⁰ Initialization of devitrification could also form points favorable to the appearance of bubbles, and the gas is manifested by a homogeneous swelling of the whole body, and the dimensions of the samples expand, and thus the bar "R" has elongated by nearly a third of its length (Fig. 43).

* Translated

LEACHING AND ALTERATION OF MINERALS

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INTRODUCTION

We know that ceramic or glass radioactive waste forms will not be thermodynamically stable phase assemblages under the physical and chemical conditions of proposed storage. The key questions are how fast are the kinetics of deterioration in the presence of radiation damage and what transport mechanisms may move undesirable components through and out of the waste forms?

Several aspects of the problem lend themselves particularly well to experimental study. These are: 1) determination of the stable phase assemblages to which the waste chemical system will tend to alter under the series of temperature, pressure, fugacity of water, oxygen, etc. environments through time; 2) determination of the permeability of the waste form to air, water, and saline solution as a function of temperature, radiation damage, and extent of mineral alteration; and 3) determination of the leachability of the waste form by aqueous solutions of varying compositions (Few, if any, geologic formations less than a km. deep remain totally unbreached by groundwater for 100,000 years:).

We have been studying a closely analogous problem, the alteration, permeability, and leachability of the warm rock that serves as a heat reservoir for geothermal systems. The same kinds of experimental approaches could be applied to test the stability of glass and ceramic waste formulations. We shall describe our apparatus and experiments using rock studies as examples.

EXPERIMENTAL STUDIES

One geothermal reservoir rock that we are studying (GT-2) is a granodiorite consisting mostly of quartz, potassium feldspar, plagioclase, and biotite that crystallized in the 700-800°C range. The rock is now at 200°C and it is 3 km. below the present erosion surface. The stable phase assemblage for its present environment is mostly quartz, albite, chlorite, potassium feldspar, and epidote. It is slowly altering to the new assemblage; at the same time the water being injected to extract heat is both speeding up in situ alteration and leaching chemical components and transporting them away.

Our laboratory consists of the following:

1. Static Hydrothermal Systems

Several cold seal pressure systems are in the final stages of construction or completed. Maximum conditions are:

- 2kb H₂O @ 800°C system with 6 vessels
- 2kb CH₄ @ 800°C system with 6 vessels
- 4kb H₂O @ 750°C system with 4 tipping vessels for rapid quench
- 7kb H₂O @ 700°C system with 6 vessels

These are used to investigate mineral phase equilibria and the kinetics of changes toward equilibria. An example is the reaction between plagioclase and 0.1 N Na₂CO₃. Two selected plagioclases of uniform composition, albite and labradorite, were each allowed to approach equilibrium in experiments from 6 hours to 3 months at 0.48kb and 200°C. Overgrowths of analcime and calcite were observed with a scanning electron microscope with a nondispersive analyzer and solution composition was monitored with time (Figure 1).

2. Agitated Hydrothermal Systems

We currently have 4 rocking vessels (700 ml) allowing maximum conditions of 0.4kb at 300°C and plan to add 4 more. These are particularly useful in observing accelerated rock reaction with various solutions. As example is a current study of



Figure 1. Anaïcime cubes and calcite rhombs appearing as alteration products on plagioclase feldspar reacted with 0.1 N Sodium Carbonate solution for 3 months at 0.48 kb and 200°C.

the reaction of granite from the GT-2 well with distilled water. Solutions and overgrowth phases are being monitored over a period of 12 months.

3. Circulating Hydrothermal Systems

A circulating system with maximum conditions of 0.35kb and 500°C is in operation at this time (Figure 2). The pressure of 0.35kb is a feature unique to this circulating system. Rock from the Jemez geothermal well is being reacted with distilled water at 0.35kb and 300°C in a long term (6 mo.) experiment. Rock and solution compositions are monitored, (Figures 2 and 3).

A new circulation system is being built which will feature a controlled temperature gradient in the reaction vessel. Granite samples will be placed along the axis of the reaction vessel. This apparatus will help define the mass transport from the cool portion (50°C) of the long reaction vessel (36") to the hot portion (300°C). Further net mass transport can be observed in the condenser and filters as in the previous system (Figure 4).

4. High Temperature Furnace

Our one atmosphere, controlled atmosphere, high T furnace is used for mineral and glass preps and alteration for conditions up to 1500°C.

5. Permeability Systems

Permeability of rock cores of geothermal interest is being measured in apparatus generating both elevated P and T. The pressure vessel in this system is maintained at elevated temperature by an external furnace. The technique consists of confining the rock slug in an elastic sleeve through which the confining pressure is exerted. A pore pressure pulse is exerted on the top of the core and allowed to decay at a given confining pressure. Maximum conditions for this system are 0.4kb at 200°C (Figure 5).

Several pore solutions have been used. Two of them, distilled water and 0.1 N Na_2CO_3 , react with the rock. In order to define these reactions, mineral oil, which proves to be chemically inert, has been used to detect innate permeability.

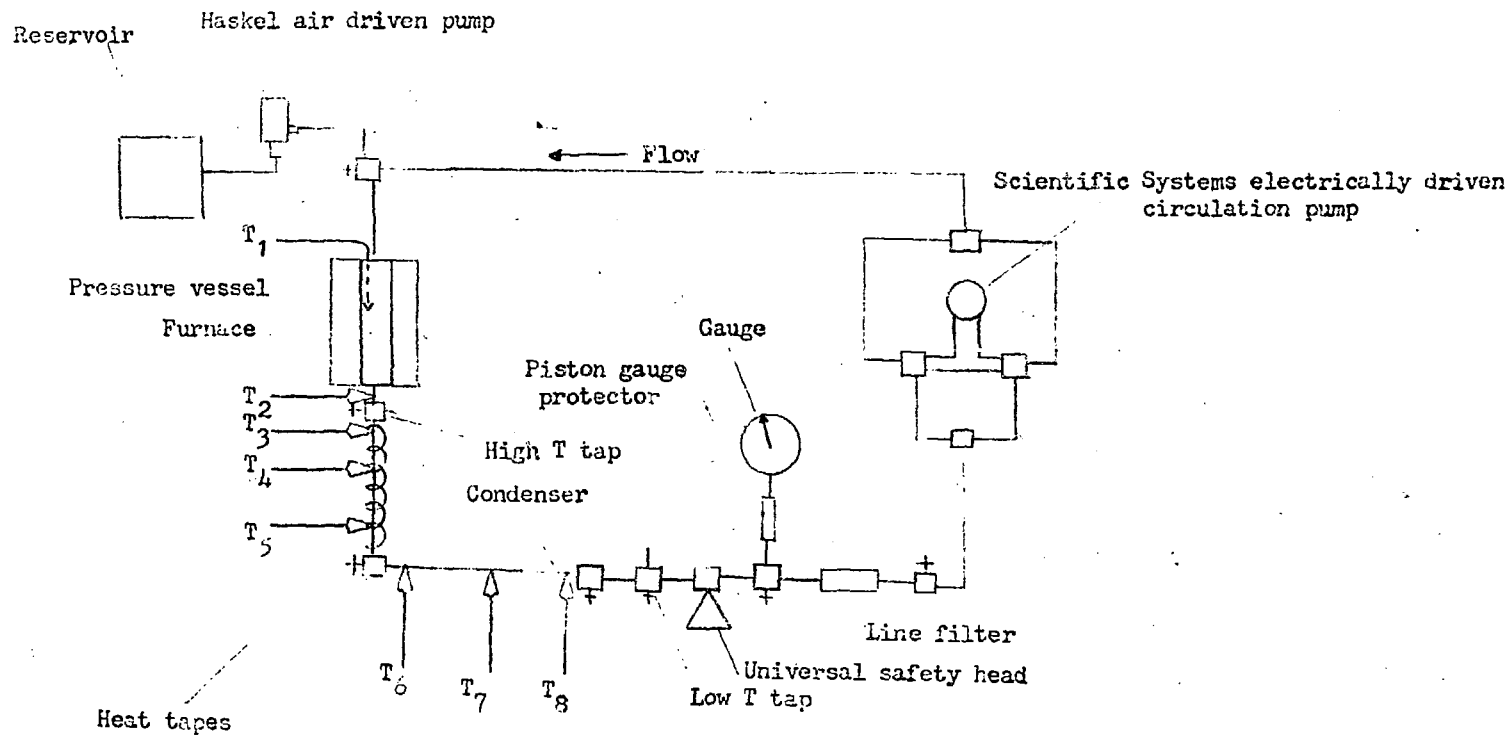


Figure 2. Second Generation Circulation System. Note: T₁₋₈ are thermocouples



Figure 3. Epidote alteration on plagioclase in granodiorite taken from the Jemex geothermal well after 3 months at 0.35 kb and 300°C. Top: 100X scanning electron micrograph. Bottom: 500X detail. The Top micrograph also illustrates erosion of grain boundary material by the circulating solution.

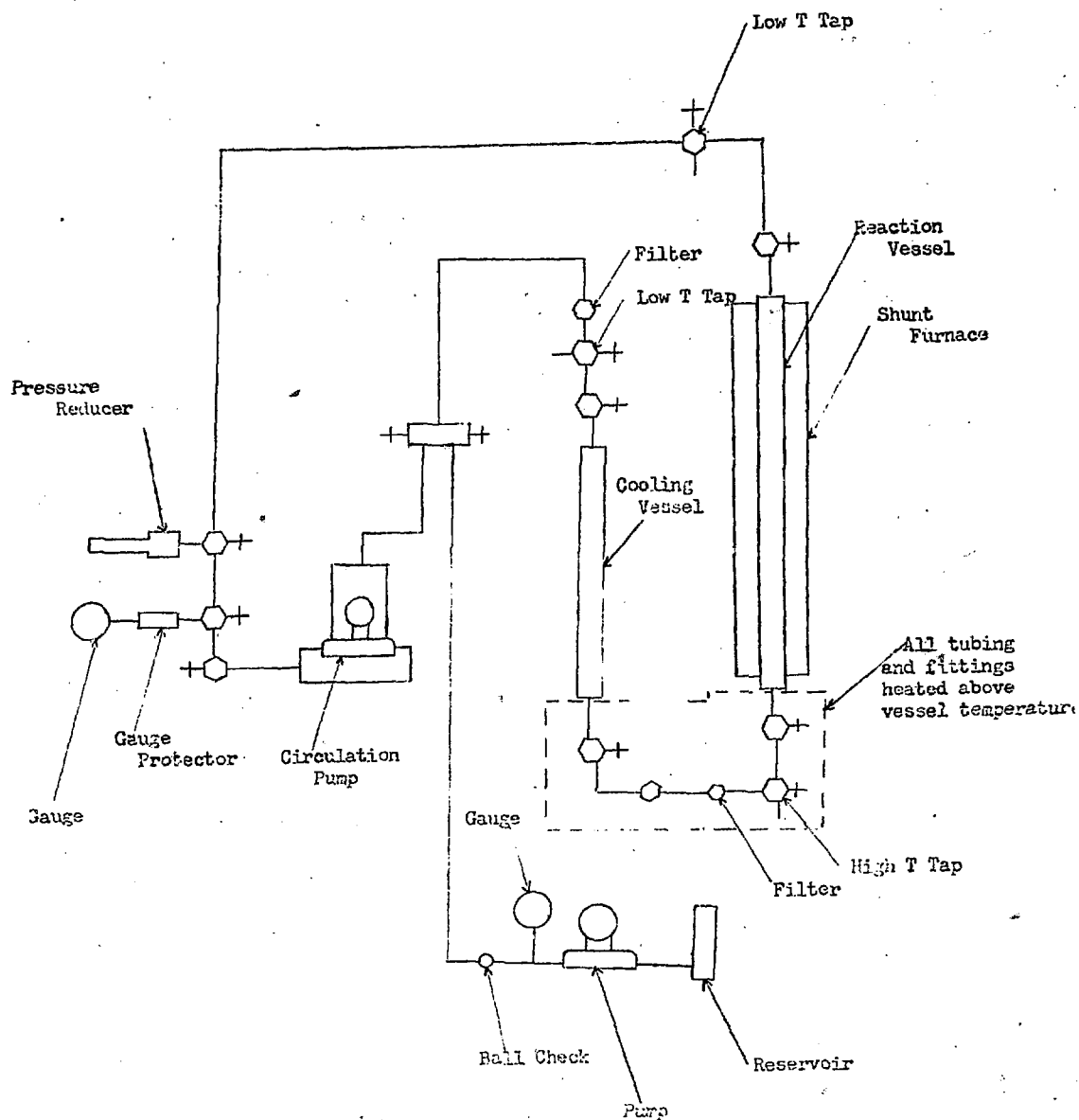


Figure 4. Controlled Temperature Gradient System

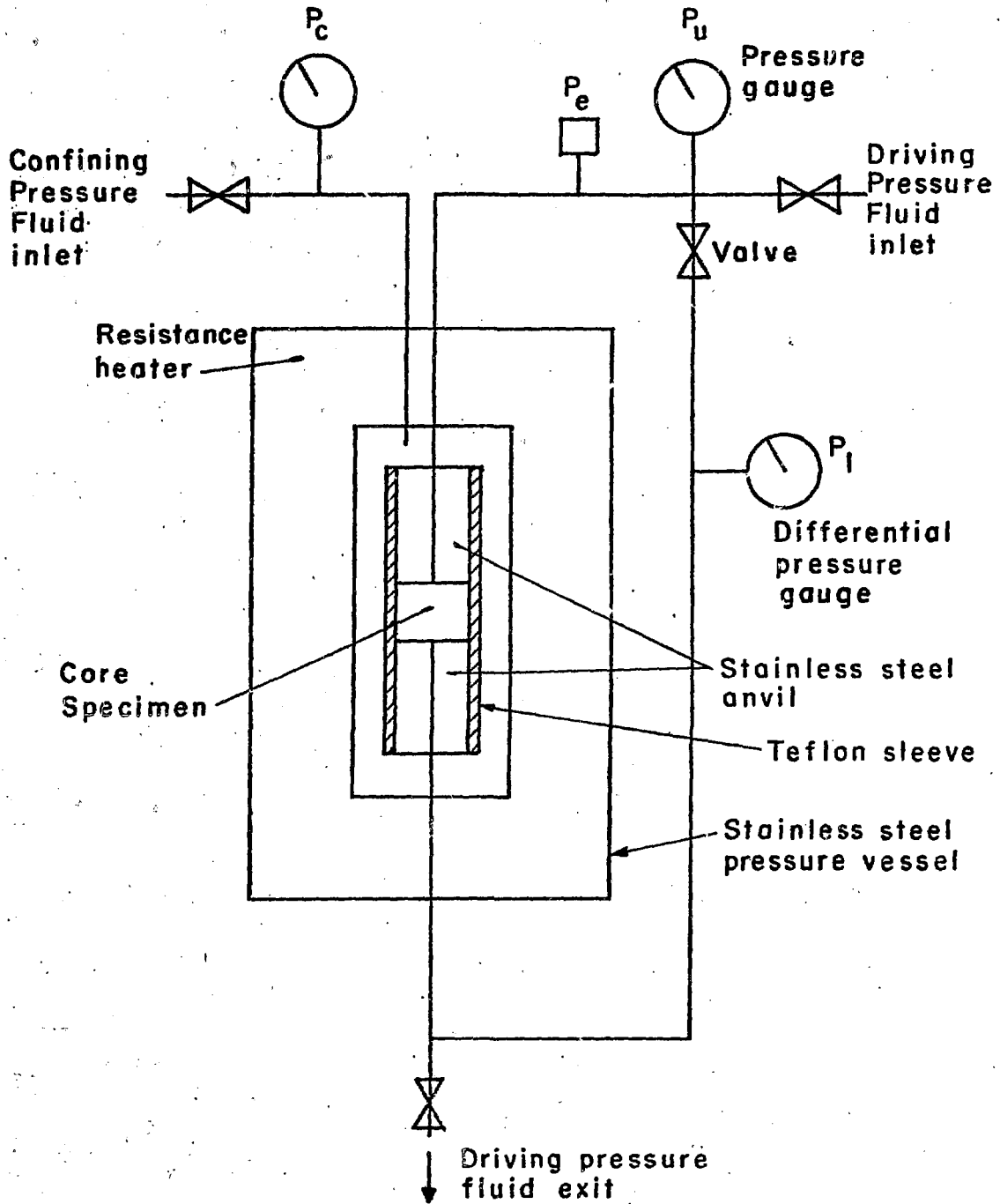


Figure 5. Permeability Apparatus Schematic

A new system is being designed which allows variation of the lithostatic load as well as confining pressure and pore pressure. Maximum conditions will be 2kb and perhaps 500°C using a copper sleeve around the rock specimen instead of teflon in the previous system.

Another set of experiments is being carried out to define the channels through which the pore solution moves. Solutions containing the radioactive species ^{57}Co and ^{35}S are forced through the core. The channels are mapped by autoradiography. This technique looks promising because fine hair-like paths along grain boundaries and microfractures can be defined, (Figures 6 and 7). The permeability and microfracture mapping of geothermally interesting rocks is being measured at this time.

6. Analytical Equipment

- . scanning electron microscope and
- . nondispersive analyzer
- . atomic absorption unit
- . neutron activation facility
- . x-ray fluorescence unit
- . hydra computer terminal
- . x-ray diffraction unit
- . electron microprobe

We have shown some experimental approaches to determination of phase chemistry, permeability, and transport that might be useful in evaluating the stability and containment potential of a glass or ceramic waste form. The effect of radiation damage on the kinetics of alteration and dissolution could also be studied experimentally by these methods.

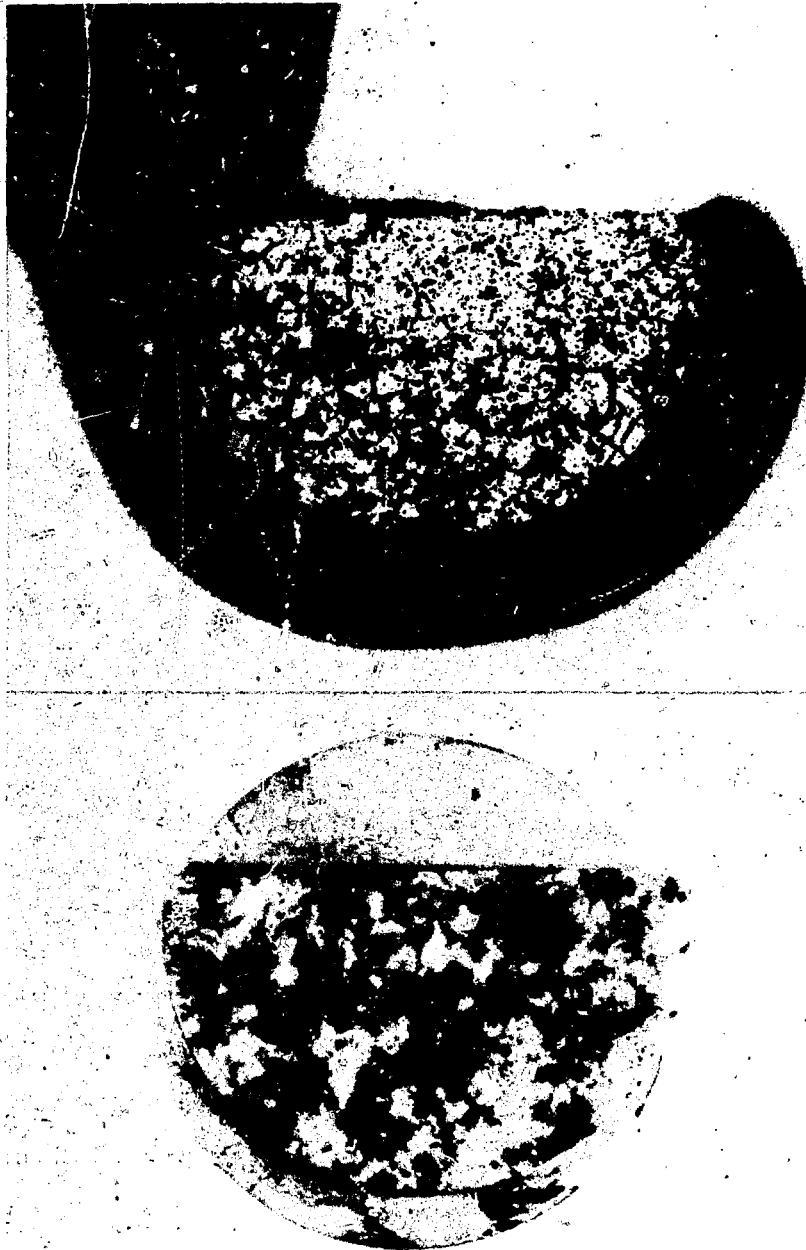


Figure 6. ^{57}Co tracer showing permeability paths in granodiorite core section
Top: Radiograph. Bottom: Photograph.

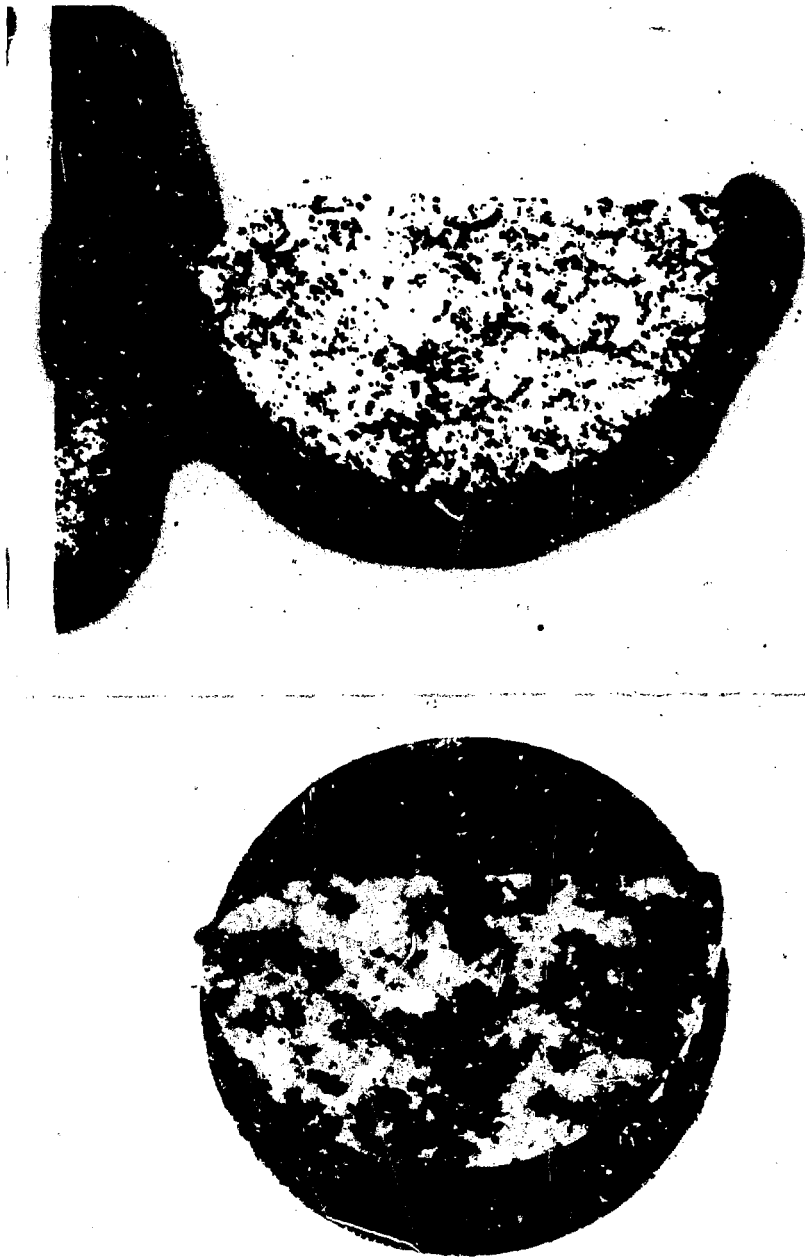


Figure 7. ^{35}S tracer showing permeability paths in granodiorite core
Top: Radiograph. Bottom: Photograph.

LEACHING OF GLASS

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INTRODUCTION

Understanding the phenomena associated with the leaching of glass is central to predicting lifetimes and performance of glassy encapsulation of radioactive wastes. The following discussion of this subject reviews the current status of understanding and controlling silicate glass surfaces primarily from the standpoint of commercial container and window glass compositions. However, progress made in understanding the importance of R_2O/RO_2 ratios, compositional additives, and the behavior of invert glasses containing <50 mole % network formers should be directly relevant to the type of glass compositional systems under development for nuclear waste encapsulation. Certainly the general theory developed for types of glass surfaces, the character, and mechanisms of film formation and dissolution offer a firm foundation for considering the leaching of waste encapsulants.

Of particular importance is the recent findings described herein that critical concentrations of soluble ions can serve to passivate the surfaces of even very non-durable glasses and prevent excessive leaching. This finding together with the other results of compositional modifications of leaching rates using only small percentages of glass additives give considerable promise for designing self-protecting glass waste encapsulation systems.

Likewise, the successful use of non-destructive surface analysis of glasses by means of infrared reflection spectroscopy gives great promise for future development of a monitoring system for ensuring high reliability of waste encapsulants.

Of equal importance is the fact that during the last few years the methodology for investigating glass surface reactions has reached a high level of sophistication. The important characterization parameters have been identified and test procedures designed to achieve precise control over environmental variables. Thus, the "guess work" has been taken out of interpreting the data.

GENERAL BACKGROUND

Considerable progress has been made in understanding the nature and behavior of glass surfaces. The Rolla Conference on Glass Surfaces and proceedings therefrom (1), firmly established that the surface-environment interactions of glass can now be treated as a science. Characterization of the composition and structure of a glass surface has been made possible through development of a number of new surface analysis techniques (Table 1). Through the use of these tools it is now a firmly established fact that glass surfaces consist of complex compositional profiles of all the constituents in the glass. Bulk composition, melt history, fabrication variables such as furnace andlehr atmospheres, and environmental history all influence the compositional profiles characteristic of a given glass article. Direct relationships between surface compositional profiles and physical and chemical properties thus can be established. In fact, it is the ability to characterize the glass surface sufficiently to relate the surface to glass processing on the one hand and glass properties on the other that makes the study of glass surfaces a bona fide materials science.

As recently reviewed (2), characterization of a glass is easy to define but difficult to accomplish, in its fullest extent. This is because of the dynamic nature and history dependence of glass structure.

Characterization of a glass surface is compounded in difficulty by the history dependence of the bulk as well as a second history dependence of the surface. To illustrate, the surface character of a float glass window pane in service depends

Table 1

INSTRUMENTAL TECHNIQUES FOR ANALYZING GLASS SURFACES*

<u>Outer Surface Methods</u>	<u>Depth of Analysis</u>
Electron Spectroscopy for Chemical Analysis (ESCA)	5-20 Å
Auger Electron Spectroscopy (AEC)	5-20 Å
Ion Scattering Spectroscopy (ISS)	5-20 Å
Secondary Ion Mass Spectroscopy	5-20 Å
Ion-Beam Induced Radiation	5-20 Å
 <u>Near Surface Methods</u>	
Ar Ion Beam Milling with the above techniques	5-2000 Å
Ellipsometry	<10->1000 Å
Infrared Reflection Spectroscopy (IRRS)	0.2-0.5 µm
 <u>Far Surface Methods</u>	
Electron Beam Microprobe (EMP)	1.5 µm
Scanning Electron Microscopy (SEM - with Energy Dispersive X-ray Analysis EDXA)	1.5 µm
Surface Dielectric Analysis	~1-10 µm
X-ray Fluorescence Spectroscopy	10 µm

*Based upon "Characterization of Glass" by L. L. Hench in Characterization of Materials in Research, Ceramics and Polymers, Chapter 8, Syracuse University Press (1975).

upon which side of the pane was exposed to the tin bath during forming, the annealing atmosphere, storage conditions before installation, and which side of the pane is exposed to atmospheric weathering versus the controlled interior environment, as well as climatic and cleaning histories, etc.

In order to improve our understanding of the physical chemistry of glass surfaces, the complexity of processing and application histories of glasses must be reduced as far as possible in conducting systematic laboratory investigations. Glasses with known histories must then be subjected to surface structure and glass compositional analysis. Such an approach is now being taken in a number of laboratories throughout the world. Results from several recent studies that utilize this comprehensive approach to glass surface physical chemistry are reviewed in this paper. The important problems addressed are:

- (1) Reaction mechanisms: a) general theory; b) surface dealcalization; c) rate dependence.
- (2) Accuracy of test methods: a) surface area to solution volume effects; b) relativity of accelerated durability tests.
- (3) Compositional effects: a) mixed alkali effects in glass durability; b) solution ion effects; c) role of CaO in glass durability; d) role of R_2O/SiO_2 in durability; e) role of Al_2O_3 in durability.
- Atmospheric treatments: a) tin and tin compounds; b) SO_2 ; c) fluorine compounds; d) formic acid.
- (5) Leaching of electrode glass membranes.
- (6) Bioglass bonding mechanisms.

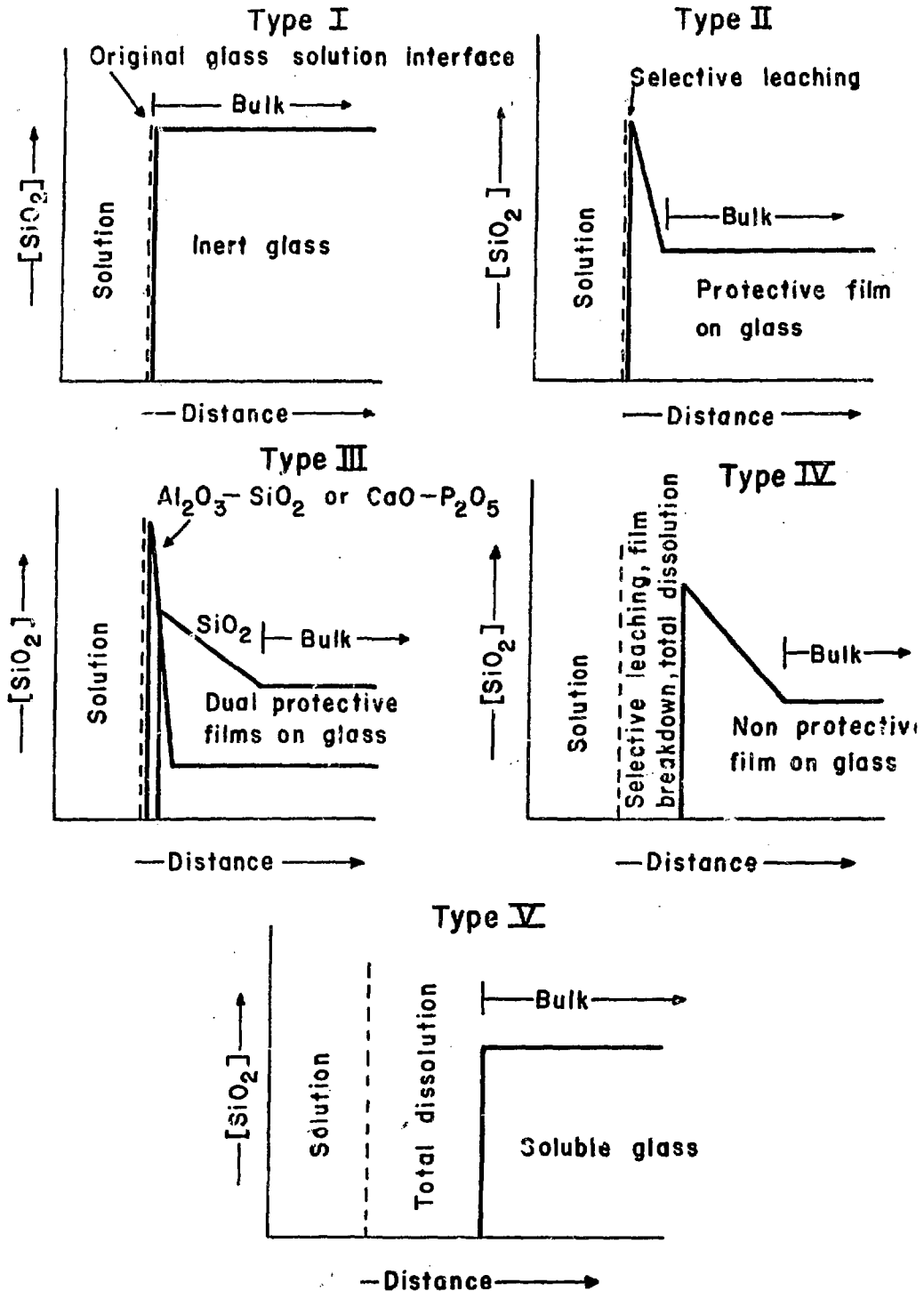


Figure 1. Five Types of Silicate Glass Surfaces Possible During Leaching

GENERAL THEORY

There are five types of surfaces which are characteristic of a silicate glass at any time in its history, Fig. 1. A Type I surface has undergone only a thin, $< 50 \text{ \AA}$, surface layer hydration. No significant surface compositional change by either dealkalization or silica network dissolution has occurred. The surface composition is nearly the same as the bulk composition. Vitreous silica exposed to neutral pH solutions has a Type I surface.

A Type II surface possesses a silica-rich protective film due to selective alkali ion removal. Dealcalization of alkali-silica and alkali-alkaline-earth silica glasses with low concentrations of alkali result in a Type II surface. A glass with this type of surface is reasonably durable, especially in solutions of $\text{pH} < 9$.

Two layers of protective surface films are characteristic of Type III glass surfaces. Adding Al_2O_3 or P_2O_5 to a glass composition can result in dual surface layers such as either alumina-silicate or calcium-phosphate species on top of a silica-rich layer. Such glasses are very durable in both acid and alkali solutions. These protective films can be produced by dealkalization, surface structural modifications or precipitation from solution.

Type IV glass surfaces also have a silica-rich film but the silica concentration is insufficient to protect the glass from rapid attack by dealkalization or network dissolution. Binary or ternary soda-silicate or potassia-silicate glasses rich in alkali form Type IV surfaces and have poor durability.

A glass that is undergoing congruent dissolution with equivalent loss of alkali and silica exhibits a Type V surface. Because of the uniform attack the surface composition of a Type V glass is equivalent to the bulk composition. Thus, there is little difference in the surface SiO_2 compositional profile between a Type V and Type I glass. However, a glass exhibiting Type V behavior is losing

considerable quantities of ions into solution. Thus, solution analysis distinguishes the two types. Also a heterogeneous attack of the surface often results under Type V conditions which is visible by various microscopy or infrared reflection spectroscopy techniques. Silicate glasses exposed to conditions with pH > 9-10 tend towards Type V behavior.

Many years of investigation have established that there are two general stages of surface reactions in alkali containing silicate glasses exposed to an H₂O containing environment (3-5). The Stage 1 reaction is dealkalinization of the surface by exchange of a H⁺ ion with an alkali ion and tends to dominate for solutions of pH < 9. At pH values of > 10, network dissolution by OH⁻ breakdown of Si-O-Si bonds tends to dominate, e.g., Stage 2. However, it is now known that both Stage 1 and Stage 2 processes can occur simultaneously over very wide ranges of pH (6). Thus, the type of surface characteristic of a glass at any particular time, e.g., Types I-V, is determined by the relative rates of Stage 1 and Stage 2 process that the glass has been exposed to in its environmental history.

Because of the complexity of the above factors it has been very difficult to establish standardized surface conditions for glasses in order to conduct unambiguous experiments. The boundary conditions are often continuously changing. However, several recent experiments discussed in the following sections have eliminated many of these uncertainties and firm conclusions can be made regarding several aspects of the physical chemistry of glass surfaces.

SURFACE DEALKALIZATION

A recent study of the surface compositional profiles of a typical soda-lime-silica container glass using Auger electron spectroscopy (AES) showed that as little as five minutes exposure to laboratory air at room temperature results in surface dealkalinization (6). A pristine bulk surface was formed prior to air exposure by ion milling. Argon ion beam milling followed by AES revealed that a SiO₂-rich layer

$\sim 500 \text{ \AA}$ thick formed in the near surface of the glass due to Na_2O and CaO migration to the glass-air interface as very thin surface film, $\sim 50 \text{ \AA}$, rich in modifier ions. Secondary ion mass spectroscopy (SIMS) of a glass of similar composition showed a H^+ ion profile that was an inverse of the sodium and calcium profile providing direct experimental evidence that dealcalization is due to a hydrogen ion-alkali exchange mechanism. Continued exposure to laboratory air for 60 minutes resulted in a silica-rich layer of nearly $1000 \text{ \AA}$ being developed. The silica concentration of the surface increased from a bulk value of ~ 75 mole percent SiO_2 to a surface maximum of 87% SiO_2 within 5 minutes and 90% SiO_2 after 60 minutes.

Thus, these experiments show that a Type II, protective film surface develops on commercial container glasses by dealcalization within minutes or less of exposure to ambient air. Other similar experiments reported in the same work (6) show that atmospheric treatments by exposure to SO_2 or fluorine containing gases primarily serve to increase the concentration and depth of the SiO_2 -rich surface layer. A Type II glass still results.

RATE DEPENDENCE OF SURFACE REACTIONS

There is general consensus that Stage 1, dealcalization reactions occur at low to intermediate pH's with a diffusion controlled square root, $t^{1/2}$, time dependence (3-5). Also, in reasonably general agreement is the appearance of Stage 2, network dissolution reactions at high pH's with an interface controlled linear time dependence (3-5). However, there has been considerable controversy over the transition between the square root to linear regimes, the extent of the transition, and the origin of it (7,8).

A recent study (9,10) has shown that the long transition period between limiting conditions of $t^{1/2}$ to t^1 rates of aqueous corrosion are observed only when glass powders are corroded, even using the Sykes method (11). A series of experiments with powders of different surface area to volume (SA/V) ratios show

that the long transition period is due to concentration cell effects in the powders which locally increase the effective (SA/V) ratios causing a rapid increase in the pH surrounding many of the glass grains. The corrosion kinetics observed for the total solution is a mixture of the glass grains in a dilute solution having $t^{1/2}$ kinetics with those in a local high pH solution having t^1 kinetics.

Corrosion of polished bulk glass surfaces using static corrosion cells does not produce concentration cell effects (12). Bulk glass aqueous corrosion shows a precise $t^{1/2}$ dependence up to pH = 9-10 for both alkali and silica leaching from binary lithia-silicate (9,10). Soda-silicate (9,10,13), and commercial container glass compositions (6). At a pH between 9-10, dependent upon composition, a sharp break in kinetics to a t^1 behavior occurs for both alkali leaching and silica dissolution for all systems studied using the bulk planar surface method. Thus, the change from diffusion controlled Stage 1 to interface controlled Stage 2 network dissolution primarily depends on the time required for the pH to reach a value where the protective Type II silica-rich film starts to become depolymerized. Previous complex kinetics analysis of glass surface reactions (14) therefore do not appear necessary to account for a transition process.

SURFACE AREA TO SOLUTION VOLUME EFFECTS

The previous section indicates that test methods can seriously affect the accuracy of glass durability studies. Use of glass powders has been a standard method for many years (15). However, even when using the ether washing procedures of the careful Syke's technique (11), agglomerates of large particles may still be present, concentration cell effects exist, and precise measurement of surface area of the glass grains is nearly impossible. The fresh fracture surface quickly undergoes the initial stages of dealcalization and compositional and structural characterization of the grains cannot be followed. Also film formation on smaller particles greatly alters the effective surface area for further reactions and this

error becomes more severe the longer the exposure time until the smaller particles are totally dissolved.

For the above reasons, studies of aqueous and weathering reactions on freshly ground (600 SiC grit) bulk glass surfaces are preferred. However, control over the ratio of glass surface area (SA) exposed to the solution volume (V) is absolutely essential. Several investigations have firmly established that as the (SA/V) ratio increases the corrosion rate increases for static corrosion conditions (6,9,10,13). The (SA/V) ratio can be increased by decreasing the depth of a corrosion cell exposed to a flat glass sample, by placing two plates close together with a thin solution film between them, or increasing the roughness of the surface of the glass plates.

Profilometer traces of glass plates polished with 600 grit SiC paper show a surface roughness of ± 3 microinches whereas a 120 grit polish shows a roughness ± 30 microinches (13). Therefore the (SA/V) ratio of the 600 grit glass samples studied by Sanders and Hench (12,16) was 0.77 cm^{-1} , but the 120 grit polished surface had a (SA/V) of 1.42 cm^{-1} (16). A recent study showed that the increased rate of corrosion due to the deeper surface scratches is directly proportional to the increased (SA/V) ratio of the rougher surface (13).

Studies of commercial glass weathering (6) showed that under (SA/V) conditions of 0.77 cm^{-1} nearly 1 day was required for dealcalization to increase the solution pH to > 9 . However, when the glass plates were in intimate contact and (SA/V) was $> 100 \text{ cm}^{-1}$ the pH became > 9 within a few hours. Infrared reflection spectroscopy and scanning electron microscopy of the weathered surfaces (6) showed only little structural attack at the 0.77 cm^{-1} condition after 20 days but extensive attack and surface roughening under the $> 100 \text{ cm}^{-1}$ (SA/V) conditions.

Thus, it is essential to control (SA/V) ratios when conducting either aqueous corrosion or weathering tests. It is easier to control this ratio using bulk planar

glass surfaces than powders. The data also show that increasing (SA/V) is a valid means of accelerating the rates of static attack of glass surfaces (6,13). Both Stage 1 and Stage 2 reactions occur in such tests but the kinetics are simply accelerated because the critical pH where Stage 1 $\rightarrow$ Stage 2 occurs much more rapidly in a high (SA/V) condition.

RELATIVITY OF ACCELERATED DURABILITY TESTS

As discussed above, increasing (SA/V) ratios provide a valid means of accelerating glass surface reactions. Many acceleration techniques in common use today pose severe problems, however.

Acceleration of reactions by using fine powders has the inherent problem of controlling (SA/V) throughout the powder as described above, or eliminating trace contaminants from sieves, or prevention of heterogeneous attack at air bubble-powder interfaces. Fractured powder surfaces also do not represent the actual glass article being evaluated.

Acceleration of surface reactions by use of elevated temperatures is a valid procedure, as described by Lyle (17), up to 95°C. However, a recent study has confirmed Lyle's conclusion that the rate constants must be established for each compositional system (10).

Increasing temperature and pressure as proscribed in autoclave tests (15) is not a valid acceleration procedure because the surface reaction processes are altered. In a recent study (6), commercial container glasses were exposed to conditions fulfilling requirements of the ASTM durability test, C225, method B-W. The (SA/V) for this test is very low and approximates infinite dilution of the extract, thereby minimizing changes in solution chemistry. The 121.5°C exposures were carried out in an autoclave at 14-15 psi for 1 hour. Auger electron spectroscopy and Ar ion beam milling were used to obtain composition profiles of the glasses after the autoclave treatment. The post autoclave profiles were

compared with profiles after 1 hour exposure to 37°C pure water of neutral pH. The room temperature water treatment leached sodium to a depth of 400-600 Å and calcium to a depth of 100-200 Å resulting in a silica-rich surface film ~100 Å thick.

The autoclave treatment however resulted in a surface profile with considerable less depletion of both sodium and calcium. It is proposed (6) that the autoclave conditions shift the surface reactions from Stage 1, dominant in 37°C water, to Stage 2 reactions. Hydrated silica has a very low solubility in neutral solutions at 37°C but the solubility increases dramatically with temperature (18). Thus, the room temperature exposure leads to dealkalization and a hydrated silica surface whereas the hydrated silica goes into solution during 121.5°C autoclave treatment along with calcium and sodium species. The difference in reactions between the two temperatures was confirmed by solution analysis which showed silica in the high temperature solution but not in the 37°C solution. A previous study (19) also showed that high temperature autoclave treatments can even lead to surface crystallization of hydrated metasilicates if insufficient solution is present. Thus, acceleration of glass durability tests by high temperature autoclave environments does not accurately represent the sequence of surface changes occurring during low temperature aqueous exposure of the glass.

MIXED ALKALI EFFECTS IN GLASS DURABILITY

It has been known for many years that glasses with certain ratios of $\text{Na}_2\text{O}/\text{K}_2\text{O}$ exhibit a corrosion rate that is less than that for glasses of equivalent alkali content with only Na_2O present (20,21). This phenomena is commonly referred to as the mixed alkali effect (MAE) in durability. A recent investigation has shown that the MAE occurs only when certain specific conditions are met (13,22). When mixed alkali glasses are corroding under Stage 1 conditions, e.g., $\text{pH} \leq 9$, the MAE is present. This is because the MAE lowers alkali ion mobilities and therefore only influences the dealkalization process. When the corrosion solution reaches a pH

value > 9 and Stage 2 dissolution begins to dominate, the MAE diminishes and eventually is not apparent in static corrosion conditions with congruent dissolution of the glass. Since the pH of the corrosion solution of mixed alkali glasses is a function of corrosion time, solution replenishment, temperature, (SA/V) ratio, glass composition and especially RO concentration and R_2O/RO_2 ratio, the MAE depends on all of the above variables as well. Under certain combinations of solution variables bulk glasses do not exhibit any minima in durability with mixed alkali ions. Powders and bulk glasses of the same mixed alkali composition often show very different magnitudes of the MAE due to the (SA/V) effect which controls the rate of pH change.

SOLUTION ION EFFECTS

A series of experiments comparing glasses containing mixed alkali ions in the glass structure versus mechanical mixtures of glasses containing the end member alkali-silicates showed that a significant fraction of the MAE is due to solution ion effects (13,22). The presence of Na_2O and K_2O together in solution serves to lower the rate of surface dealcalization. The MAE effect with the ions only in solution is not as large as having them both in the glass and being lost to the solution. However, both contributions are important.

Other solution ion effects studied using bulk planar surfaces and constant (SA/V) ratios showed that various salt compounds promote the ion-exchange reaction and prevent total dissolution (13). The influence of the salt compounds in improving durability are, in decreasing order: $CaCl_2$, $ZnCl_2$, $AlCl_3$. Ca^{+2} ions in solution improve the corrosion resistance of binary alkali-silicate glasses by a factor of 10 in comparison with pure water. $CuCl_2$ increased the total dissolution rate.

A detailed study of Al^{3+} ions in solution, as AlCl_3 , on the corrosion of binary $\text{Li}_2\text{O-SiO}_2$ glasses showed two distinct regions of dissolution behavior dependent upon Al^{3+} solution concentration (13,23). For concentrations ≤ 25 ppm AlCl_3 glass dissolution increased due to a more rapid increase in dealcalization and resultant solution pH. This is due to insufficient Al^{3+} ions to passivate active surface sites and incomplete formation of stable alumino-silicate surface complexes. Hence total dissolution was enhanced due to higher pH for these solutions. However, at concentrations > 25 ppm Al^{3+} the total dissolution of the glass, Stage 2, was greatly reduced although the rate of selective leaching was unchanged. AES analysis revealed that the Al^{3+} ions diffused into the glass surface to a depth of $\sim 300 \text{ \AA}$ in addition to adsorbing on the surface. Thus, sufficient concentration of Al^{3+} in solution creates a dual protective film, Type III, glass surface. Other soluble Al salts, $\text{Al}(\text{NO}_3)_3$, and $\text{Al}_2(\text{SO}_4)_3$ all showed equivalent behavior also indicating that Al^{3+} is the species responsible for forming the surface stabilizing layer.

ROLE OF CaO IN GLASS DURABILITY

Substitution of 10 mole % CaO for 10 mole % SiO_2 in a 20 mole % Na_2O -80 mole % SiO_2 glass produces a remarkable improvement in glass durability. In fact, this compositional effect is the basis of the bulk of the commercial glass industry. A recent paper (24) and book (6) has examined the surface chemical changes resulting from the CaO substitution using solution analysis, IRRS, EMP, and AES techniques. It was shown that both glasses, 20 Na_2O -80 SiO_2 and 20 Na_2O -10 CaO -70 SiO_2 , develop alkali depleted layers as a result of preferential dissolution of Na.

After one hour of corrosion, the majority of the Na has dissolved from the surface of the binary glass and complete breakdown of the SiO_2 -rich layer has begun. However, a significant quantity of Na is still present in the ternary glass containing CaO corroded for 12 hours. After 2 days, Na is not detectable with IRRS,

and local breakdown of the structure as the result of pitting is observed. The slight increase in the IRRS Si-O-Si peak for 5 days results from the continued depletion of Na, producing a layer that is rich in both Si and Ca. The increase of Si in solution is accompanied by an increase in pH, surface roughening, and a decrease in the IR Si-O-Si peak height and Si X-ray intensity after 9 days, suggesting a uniform breakdown of the SiO₂-rich structure present on the glass surface.

Compared with the binary glass, the decrease in the early-stage corrosion rate for the ternary glass could be interpreted as an increase in coupling interactions between Si-O-Si and NS bonds influenced by the presence of the CaO modifier. The stronger structural coupling retards the dealkalinization of the glass. However, in the later stage of corrosion the ternary glass develops a CaO-enriched zone within the Na-depleted, silica-rich layer. The CaO apparently stabilizes the SiO₂-rich surface film by filling the microvoids, satisfying the bonds, and forming a chemical barrier to further Na diffusion.

ROLE OF R₂O/SiO₂ IN GLASS DURABILITY

An equivalent set of experiments to that described in the previous section has been recently reported (6) for the following Na₂O/SiO₂ ratios: 10/80, 10/70, 20/80, 20/70, 20/60, 30/60, 14.5/85.5, 14.5/75.5, 14.5/72.5, and 15.2/71.5. The general findings of this study were that a low Na₂O/SiO₂ ratio results in formation of a Type II surface; a high Na₂O/SiO₂ ratio produces a Type IV surface. Substitution of 10 mole % CaO for 10 mole % SiO₂ decreases Na dissolution for all Na₂O/SiO₂ ratios but is most effective when the mole % of Na₂O is not greater than 15%.

Weathering studies (6) of glasses of the same Na₂O/SiO₂ ratios listed above show that the rates of surface precipitate formation and SiO₂ film development increases as the percentage of Na₂O increases. The resistance to weathering with and without water condensation is directly dependent on the SiO₂ content of the

glass. For example, the extent of weathering after 28 days is approximately the same for both 20 Na₂O-10 CaO-70 SiO₂ and 10 Na₂O-20-70 SiO₂ glasses. Increasing the total quantity of Na₂O + CaO above 20 percent drastically reduces the weathering resistance. IRRS analysis showed the mechanism of weathering attack is primarily Na ion decoupling from the network and is most severe when water condensation and runoff occurs. The rate of Na decoupling in condensation weathering is even more severe than in aqueous corrosion at the same temperature. This is attributed to the continual wash off of the protective Ca-rich film during weathering and continuous removal of the Na ions from the surface layer. Thus, continuous removal of the protective surface layer of a Type II glass forces it towards a Type V surface.

ROLE OF Al₂O₃ IN GLASS DURABILITY

The effect of 0-11 mole % Al₂O₃ additions to binary Li₂O-SiO₂ glasses has been studied using solution analysis, IRRS, and AES-ion milling techniques (13,25). The first 2.5% Al₂O₃ addition has the greatest effect on decrease Si⁴⁺ dissolution. Li⁺ leaching decreased in proportion to the % Al₂O₃ present. Adding the alumina to the glass significantly reduced the importance of pH in glass dissolution and increased the pH for the transition from Stage 1 to Stage 2 reactions from a value of pH 9 to pH > 10. A ternary composition analysis of the static corrosion solutions using solution parameters α and ϵ (12) showed that in early stages of corrosion, selective leaching of both Li⁺ and Al³⁺ ions occurred with the corrosion path headed in the direction of total dissolution. For alumina additions > 2.5% there was a reversal in the compositional path during the later stages of corrosion. This is indicative of the precipitation of an alumina-silicate complex from the corrosion solution onto the glass surface. Auger electron spectroscopy confirmed the formation of the alumina-silicate corrosion film formed on top of the silica-rich layer resulting from dealkalization. Films of 300 Å were formed. Thus, a Type III glass surface is produced with the Al₂O₃ additions. It is the two layer protective film that is

responsible for the high durability of glasses containing Al_2O_3 . The double film prevents selective leaching and greatly slows the rate of total dissolution. Comparison of the surface films formed by adding the Al_2O_3 in the glass versus adding Al^{3+} ions in solution shows that 100 ppm Al^{3+} in solution is equivalent to 3 mole % in the glass. Alumina-silicate films formed in either manner provide equivalent resistance to aqueous corrosion.

EFFECTS OF TIN ON GLASS SURFACES

Auger electron spectroscopy has been used by Chappell and Stoddart (26) to establish that unweathered float glass possesses an excess concentration of tin on both the bottom and top side of the glass. The tin concentration was about 10 times greater on the bottom and was accompanied by iron contamination as well.

Sieger has also shown that the top and bottom surfaces of float glass are chemically different from the bulk glass composition (27). Electron microprobe and X-ray fluorescence-HF etching techniques were used to obtain compositional gradients. Tin oxide was found in a greater concentration in the bottom surface of the glass than at the top. The concentrations of Na_2O , CaO and SO_3 are lower at the top surface than in the bulk glass, while SiO_2 is higher. Complex concentration gradients and variable oxidation states are found between the two surfaces.

In a separate study (28) it has been found that the top surface of float glass is considerably stronger than the bottom surface. However, water immersion and/or abrasion reduces the strength difference between the top and bottom surfaces.

Glasses exposed to SnCl_4 vapor or SnCl_4 /butyl acetate spray at temperatures of 450-650°C develop tin oxide surfaces. Budd (29) has found using ESCA analysis that two forms of stannic tin were present on the surface, one assigned to SnO_2 and the other in a form associated with one or more glass elements. The concentration of the SnO_2 form of tin is greatest at the surface, while the matrix bonded form has maximum concentration in the subsurface. The relationship between these findings

and mechanisms of improvement of durability has yet to be established. Formation of a dual protective layer Type III glass surface is likely.

SO₂ TREATMENTS

Anderson, et al. (30), have conducted a thorough analysis of the surface compositional changes accompanying SO₂ vapor treatments of a typical container glass. Depletion of sodium to a depth of ~ 2000 Å was indicated by the solution analysis. ESCA showed a large sodium depletion to a depth of 400 Å (the greatest milling depth employed). Substantial depletion of calcium was observed to a depth of 2000 Å by AES. Durability testing was performed at 121°C for 1 hour according to ASTM C225-73, method B-W using rinsed bottles filled with water or 1% KHCO₃ solution. The composition of the extracted solution obtained from the durability test was that of the bulk glass composition even for treated bottles. However, the total amount of extraction was substantially reduced by the SO₂ treatment.

As discussed above in the section on accelerated testing, the autoclave test tends to force the surface into Stage 2 processes with network dissolution. The process is not stopped even with the surface depletion by the SO₂ treatment.

In another investigation of the effects of SO₂ treatment using AES (6), it was also found that the sulfur treatment serves to deplete the surface almost entirely of CaO and Na₂O resulting in a 100% SiO₂-rich surface to a depth of 50-75 Å, which is perhaps the compact silica layer hypothesized by Douglass and Isard (31). The important consequence of the thorough soda and silica modifier depletion is the elimination of ambient weathering from the sulfur treated surface and an extreme resistance to hydration and leaching during the 1 hour ASTM durability test. However, as found by Bacon (32) and Persson (33) in their long term corrosion studies, the SiO₂-rich layer is still subject to eventual hydration with consequent exchange of hydrogen and sodium ions. Thus, under long term static corrosion conditions even such Type II, protective barrier surfaces will degrade to a Type V

dissolution state when the pH becomes sufficiently alkaline. However, the kinetics of Type V dissolving surfaces are strongly dependent on glass composition. Recent studies by several investigators have shown that the rate of change from Stage 1 to Stage 2 reactions and Type II to Type V surfaces is primarily a function of bulk SiO_2 content and ratio of surface area of glass to volume of solution exposed to the glass (6,10,13).

EFFECTS OF FLUOROCARBON GAS TREATMENTS

Anderson, et al (30), also investigated the surface compositional changes resulting from passing a commercial container glass under a mixture of 1, 1 difluoroethane and air. There were no detectable amounts of fluorine in the water extract or in the AES or ESCA spectra of the unmilled surface of the fluorocarbon treated bottles. This led to the conclusion (30) that the enhanced chemical resistance from such treatments by fluorine replacement of hydroxyl and/or oxygen groups can involve at most a minor fraction of such groups. A substantial depletion of calcium to a depth of 500-1000 Å was detected by both AES and ESCA. Depletion of sodium was also shown by ESCA.

A separate investigation (6) of fluorocarbon gas treated containers using AES also could not detect fluorine in the glass surface before or after ion-milling. In contrast, it was shown that exposing the surface to a 5% HF solution, followed by a water rinse, did result in detectable fluorine by AES to a depth of ~ 50 Å. Thus, fluorine does ion exchange with commercial glasses and can be detected by AES, but apparently does not substitute within the glass surface structure when exposed as a fluorocarbon gas. A substantial depletion of sodium and calcium from the surface to a depth of 150 Å was determined by AES. The compositional profile was very similar to that found for sulfur treated bottles, see above. Apparently, the role of the fluorine is one of catalyzing high temperature dealcalization by ion exchanging with oxygen or hydroxyl ions. The fluorine perhaps then combines

with Na and Ca in the surface and vaporizes as NaF and CaF species. The resultant dealkalized surface region then becomes compact, forming a fused silica-like surface layer that provides high corrosion resistance.

ORGANIC ACID VAPORS

Tsuchihashi, et al (34), have used optical microscopy, X-ray diffraction, EMP, and ellipsometry to characterize the surface structural changes occurring from formic acid-weathering of optical glasses. They found that in glasses with a SiO_2 network that diffusion of Pb^{2+} and formation of fine lead formate crystallites are responsible for staining. Thus, a deleterious Type III surface is created. In glasses with a B_2O_3 network, the B_2O_3 network is attacked and destroyed by formic acid solution leading to boric acid crystallites and a Type V surface behavior.

LEACHING OF ELECTRODE GLASS MEMBRANES

The combined work of Bach (35,36) and Baucke (37,38) is an excellent illustration of the value of surface compositional characterization in understanding complex glass surface physical chemistry phenomena. The ion-sputtering method for determining surface compositional profiles of glasses, developed by H. Bach (35,36), involves measuring characteristic ion luminescence lines of the spectra of free atoms or ions sputtered from the glass surface. Bach has used this method to determine that interdiffusion between surface coatings and glass substrates extends over $\sim 1000 \text{ \AA}$ thick regions (36).

Baucke has used the ion-sputtering method to show the formation of leached surface layers on pH-glass electrode membranes (37,38). He has shown that pH and temperature dependent lithium concentration profiles become constant after a certain leaching period and attain a characteristic form which can extend into the glass to a depth of $> 1000 \text{ \AA}$. The depth of surface depletion is significantly less, $\sim 300 \text{ \AA}$, for low temperature, 5°C , leaching than for 75°C leaching, $> 1000 \text{ \AA}$.

Alteration of the solution temperature and pH of the electrode membrane during use produces a complex combination of Stage 1 leaching and Stage 2 film dissolution that eventually reaches a steady state leached Li composition profile dependent upon past history and new environment. The Type II surface character accounts for the high electrical resistivity of the membrane surface layer (39). Proton exchange within the leached layer is associated with establishing the equilibrium pH sensitivity of the electrode with mechanistic details still controversial (38).

MECHANISMS OF BIOGLASS-BONE BONDING

An extensive investigation of corrosion reactions of an invert soda-lime-silica glass containing P_2O_5 (45 SiO_2 , 24.5 CaO , 24.5 Na_2O and 6 P_2O_5 wt %) has been conducted because of the incredible property of the glass to form a strong and stable bond with living bone (40-43). Nearly all surface characterization methods listed in Table 1 have been used to understand this phenomena. The secret of the biological success is attributable to the formation of a stable calcium phosphate film on the surface of the material (termed bioglass) when in contact with an aqueous environment. Bioglass stability directly results from formation of a Type III surface. The calcium phosphate film incorporates organic constituents as it grows. Sodium ion migration from the surface first occurs, forming a silica-rich film on the glass surface. The calcium phosphate film develops on the solution side of the silica-rich film and incorporates organic constituents such as collagen and mucopolysaccharides from the body fluids. With time (one to six weeks) the calcium phosphate crystallizes to form fine-grained polycrystalline apatite agglomerates which bond the glass surface to the newly growing bone. The presence of the calcium phosphate layer and the silica-rich film protects the bulk glass from further attack. Consequently, this material can serve as a true "biological glue" even when applied as a thick film coating to other ceramics.

Studies of additions to the P_2O_5 -containing glass show that the rate of calcium phosphate film formation can be accelerated with B_2O_3 substitution for SiO_2 or reduced and stabilized with CaF_2 substitution for CaO . Additions of small percentages of Al_2O_3 or decreasing the Na_2O/SiO_2 ratio in the bioglass also slows down the rate of surface reaction.

SUMMARY

Understanding surface compositional profiles of glasses over a range of 0-2000 Å with a variety of analytical instruments show that five general types of glass surfaces exist. The surface character of a glass article depends upon bulk composition and environmental history during which surface dealcalization, film formation, and network dissolution can occur. Environmental-surface interactions generally result in complex compositional profiles of all the constituents in a glass. Durable glasses almost always develop a stable surface film which has a higher concentration of network formers than the bulk composition. Compositional effects that are used to improve glass durability usually improve the stability of the surface films. Durability tests or service conditions that lead to film destruction are especially severe for the most silicate glasses.

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MECHANICAL PROPERTIES OF GLASS

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INTRODUCTION

An essential prerequisite to the use of nuclear fission as a major method of producing electrical energy is safe disposal of radioactive wastes (1). To avoid contamination of the ecology, high-level radioactive wastes must be permanently immobilized under almost any foreseeable circumstance. One method that has been proposed for such waste disposal is encapsulation of the wastes in glass, which will then be stored in stainless steel containers and buried in safe locations (1). To dispose of wastes in this manner, the glass must maintain its mechanical integrity to resist corrosive attack in the eventuality that the steel containers are penetrated by water. Thus, it is essential to understand the mechanical properties of glass as they relate to problems of waste disposal.

Brittle behavior is the most characteristic mechanical property of glass. When subjected to mechanical loads glass does not deform plastically; instead it deforms elastically until a critical load is reached. At this point the glass fractures, often into many small fragments which increases its surface area and enhances its susceptibility to corrosive attack by water. This fracture behavior is further complicated because glass is susceptible to stress corrosion cracking which results in delayed failure often after glass has been subjected to mechanical stresses for considerable periods of time. Thus, fracture and fragmentation can occur after waste materials have apparently been safely encapsulated in a glass matrix.

Time dependent stresses can also cause delayed failure of glass. These stresses arise from several sources: from thermal gradients that occur as the glass is cooled from the casting temperature; from heat generated as a result of radioactive decay of waste products; and from phase transformations caused by thermodynamic instabilities of the glass composition. The stress fields generated by these processes will increase the possibility of fracture after encapsulation of waste materials and hence reduce the resistance of glass to corrosive attack by water.

This paper briefly reviews the fracture properties of glass. Specific attention is paid to the manner in which these properties relate to waste disposal. Topics to be discussed include brittle fracture, stress corrosion cracking and methods of characterizing strength in the presence of a variable stress field. By understanding the underlying science of the strength of glass, and by using this knowledge to formulate glass compositions and processing procedures for encapsulation, it is hoped that many of the problems that are associated with nuclear waste disposal can be overcome.

BRITTLE FRACTURE OF GLASS

Strength of glass is almost completely determined by the microstructural perfection of its surface (2, 3). Glass that is free of microstructural surface flaws is very strong, and strengths as high as 2×10^6 psi have been achieved by chemical or thermal polishing to remove surface flaws (4, 5). However, when microscopic flaws or cracks are present in the glass surface, the strength is greatly reduced, because of stress concentrations in the vicinity of the flaws. Since these stresses cannot be relieved by plastic flow they increase in magnitude as the forces on the glass are increased. Fracture finally occurs when the stresses at one of the surface flaws exceed the inherent molecular strength of the glass.

The role of microscopic flaws in the fracture process was first expressed quantitatively by Griffith (6), who used an energy balance to relate the mechanical energy lost during fracture to the energy required for new surface formation. He

discovered that there was a critical load required for fracture. Below this critical load crack healing occurred, while above the critical load crack propagation occurred. Griffith's theory has been amply proven by experimental studies on glass and other brittle materials and can be used as a basis for explaining the strength of glass. Expressed in quantitative terms, the Griffith theory relates the strength, σ , to both the size of cracks, c , contained in a brittle material and the fracture energy, γ , absorbed during fracture:

$$\sigma = \frac{2 E \gamma}{\pi c}$$

The surface energy, γ , and the young's modulus, E , are the materials parameters that control fracture.

The sensitivity of glass to surface perfection can be easily explained using the Griffith relationship. Glasses that have surfaces that are molecularly perfect can be considered to contain flaws that are no larger than the molecular dimensions of the glass, say 10^{-9} m. The fracture energy of glass has been measured, and for a variety of compositions is found to be ~ 4 J/m²; young's modulus of glass is approximately 70 GPa, (7). By substituting these values into equation 1 one obtains a theoretical value of ~ 13 GPa ($\sim 1.9 \times 10^6$ psi), which is close to the values obtained for chemically or thermally polished glass (4,5) (~ 13 GPa for fused silica, ~ 3 GPa for soda-lime-silicate glass). This value of the strength is reduced considerably by the presence of surface flaws. As commercially produced, these glasses contain flaws that are of the order of 10^{-5} m in size, which reduces the strength to approximately 0.13 MPa ($\sim 1.9 \times 10^4$ psi). The effect of flaw size on the strength of glass is summarized in Figure 1, which demonstrates the sensitive dependence of strength on effective flaw size, (2). Depending on the surface perfection, glass can have almost any strength.

While surface flaws are the most important mechanical source of fracture in glass, internal flaws can also be an important cause for fracture, especially in glasses that undergo phase transformations. Rindone and his colleagues, have demonstrated the important role of phase separation to the pristine strength of glass (8). Microstructural

Table 1

RELATION OF CALCULATED GRIFFITH FLAW SIZE AND
MEASURED MICROPHASE SIZE IN $0.5\text{Li}_2\text{O} \cdot 0.5\text{K}_2\text{O} \cdot 2\text{SiO}_2$ GLASS (8)

Strength (psi)	Calculated Flaw Size (Å)	Measured Phase Size (Å)
170,000	1240	1000-2000
220,000	7400	600-1500
400,000	225	200-500
500,000	140	100-200

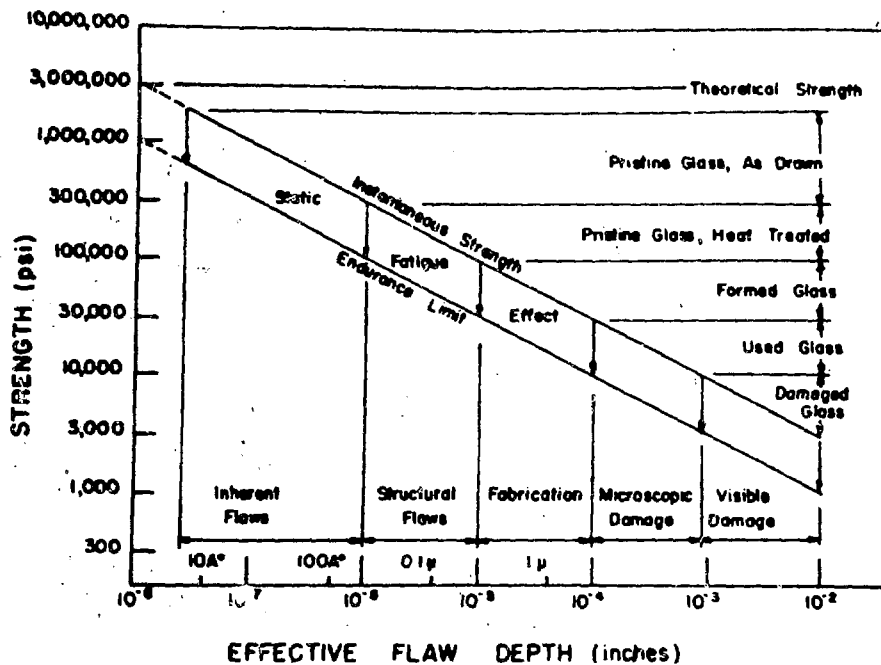


Figure 1. Effect of flaw depth on the strength of glass. The general strength ranges associated with the various flaw sizes are indicated on the figure (2).

phase changes that occurred in the melt resulted in variations of up to 50 percent in the pristine strength of glass fibers. Using the Griffith equation, these variations in strength could be quantitatively related to the size of the microphases that formed in these glasses when they were processed, Table 1. As the phase size increases, the strength was observed to decrease, a behavior which can play a dominant role in establishing the strength of phase separated glasses. Thus phase separation will have to be taken into account in any consideration of glasses for radioactive waste disposal.

According to the Griffith relationship, the fracture energy and the youngs modulus should also affect the strength of glass. For commercial glasses that are not phase separated, however, the variation of these parameters is small, Table 2, so that the ceramics formed by these processes are somewhat stronger and more resistant to crack propagation than the parent glass. Thus, phase separated glasses or crystallized glasses may be better for purposes of waste disposal. The fracture energy of glasses may also depend on other factors that have not yet been explored: factors such as radiation damage to the network structure and extreme variations in composition.* The effect of radiation damage and variations in composition should be explored to provide a broader scientific basic for selecting glass compositions for waste disposal.

STRESS CORROSION CRACKING OF GLASS

The phenomenon of stress corrosion cracking of glass is commonly known as static fatigue. The phenomenon results in a time dependent decrease in the strength of glass that must be taken into account when glass is used as a structural material. The phenomenon was first studied by measuring the time-to-failure of glass rods or bars that were subjected to a constant applied load. As the load was decreased, the time-to-failure was observed to increase (9), Figure 2, and if the load was decreased below a threshold value, failure no longer occurred regardless of the time of load

* Glasses for waste disposal contain only 30 percent silica, which is considerably less than the 60-90 percent found in most commercial glasses.

Table 2

SURFACE ENERGY AND YOUNG'S MODULUS OF GLASS AT
ROOM TEMPERATURE

<u>Glass Type</u>	<u>Young's Modulus (GPa)</u>	<u>Surface Energy(J/m²)</u>
Silica (C7940)	72.1	4.4
96% Silica (C7900)	65.9	4.0
Lead Alkali (C0041)	63.7	3.5
Aluminosilicate (C1720)	89.1	4.7
Aluminosilicate (C1723)	86.2	4.2
Borosilicate (C7740)	73.4	4.6
High Alkali Borosilicate (C7740)	81.0	4.6
60% Lead (SF1)	57.0	3.4
Soda-Lime-Silicate	73.4	3.9
Glass Ceramic (C9606)	120.0	26.6

application. This threshold is known as the static fatigue limit. Stress corrosion cracking can also be investigated by measuring the strength of glass as a function of the loading rate, in which case the glass appears to become stronger as the loading rate is increased. Data obtained by this type of measurement are known as dynamic fatigue data.

Strength effects observed in both dynamic and static fatigue experiments can be explained by subcritical crack growth in glass. In the static fatigue experiment, the time-to-failure is the time required for the crack to grow from subcritical to critical size. In the dynamic fatigue experiment, cracks are exposed to high loads for a shorter period of time as the rate of loading is increased. Hence, less sub-

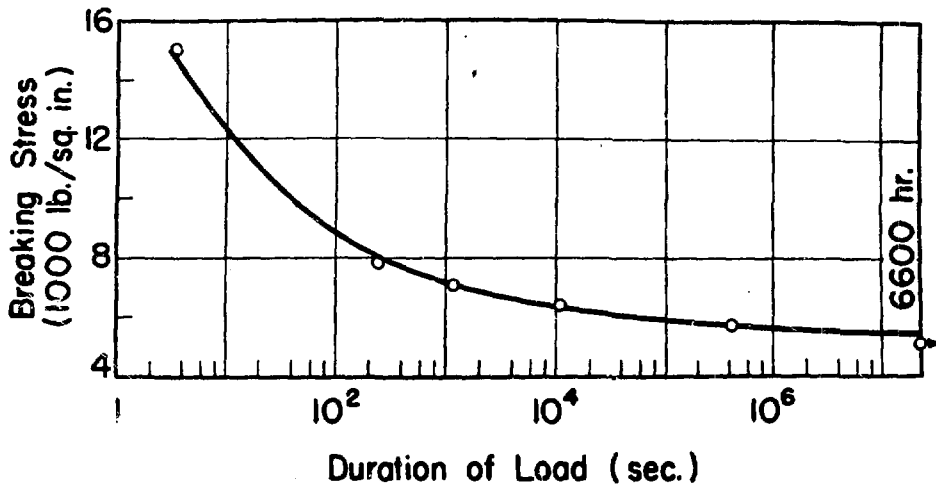


Figure 2. Static fatigue curve for annealed soda-lime glass rods, 1/4 inch in diameter (9)

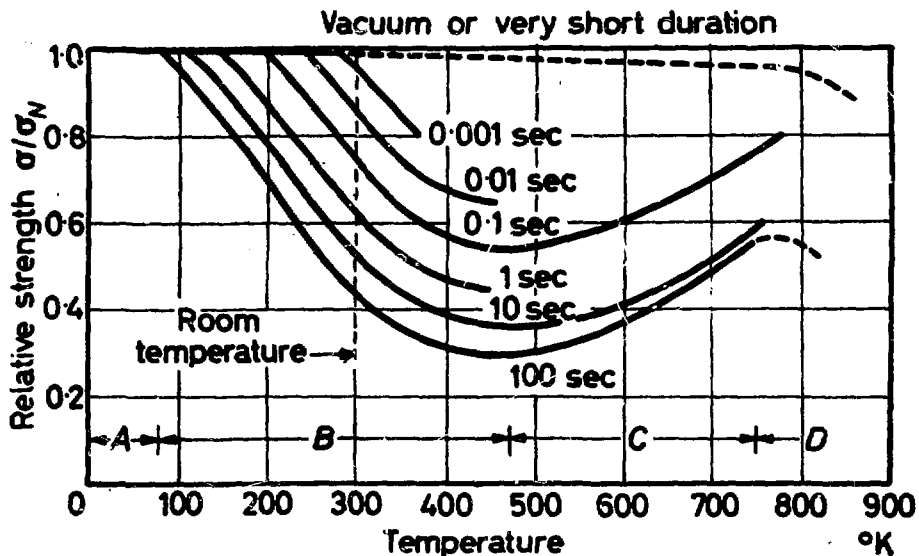


Figure 3. Relative strength of glass tested in air as a function of temperature and load duration. Semi-quantitative composite curves were collected from several investigations. The relative strength is the ratio of the applied stress, σ , to the strength in liquid nitrogen, σ/σ_N (14)

critical crack growth can occur before failure and components appear to become stronger. Since these effects are observed only in the presence of moisture, water is believed to be the main cause for the stress corrosion cracking of glass (10-13). It has been shown that very little moisture is required for the occurrence of stress corrosion cracking. (10-13).

Temperature also has an effect on the stress corrosion cracking of glass. As summarized in Figure 3 the strength behavior of glass can be divided into four regions (14). At very low temperatures, stress corrosion is so slow that there is virtually no effect of water on the fracture of glass. As the temperature is increased, the kinetics of the stress corrosion process are enhanced and for a given time-to-failure the strength is observed to decrease. A minimum in the strength occurs at approximately 200°C because water desorbs from the glass surface at higher temperatures and is not as active in promoting crack growth. At temperatures greater than ~500°C glass usually exhibits viscous flow and the strength decreases due to this flow. Figure 3 also demonstrates that in vacuum (or other inert environments) the temperature dependence is suppressed because of the low concentration of water. The effect of temperature on the stress corrosion process was also investigated by Charles (15) who observed that the fracture of glass is an activated process, Figure 4. The activation energy for the process, 18.8 kcal/mol, is close to that for the diffusion of alkali ions in glass, a result that was taken as evidence that alkali ion migration plays a role in the fracture process.

Stress corrosion has also been investigated by fracture mechanics techniques. Figure 5 is a plot of the crack velocity in water as a function of the applied stress intensity factor (16). Although the crack velocity is expressed as an exponential of the applied stress intensity factor other functions fit the data equally well. Note that the slopes and positions of the curves in Figure 5 depend on the composition of the glass studied. The data for the soda-lime-silicate glass seems to exhibit a stress corrosion limit, a result that is consistent with that obtained by strength

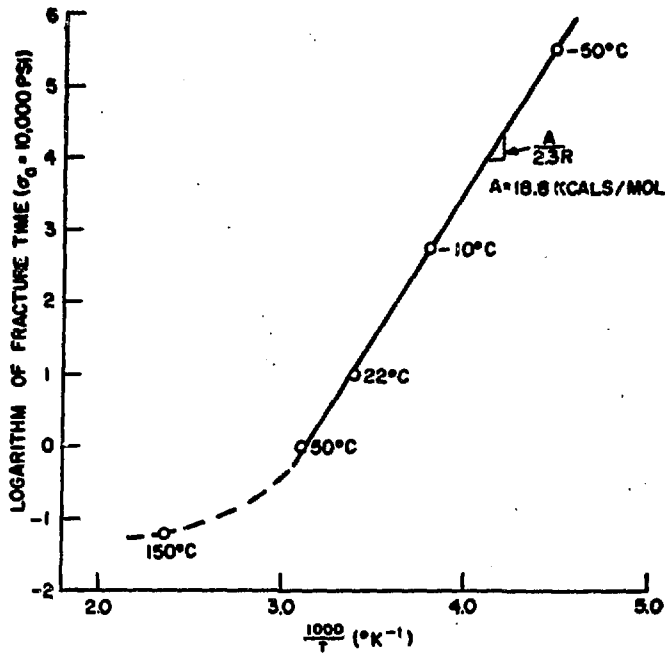


Figure 4. Temperature dependence of static fatigue process. The applied stress was ~ 70 MPa (15).

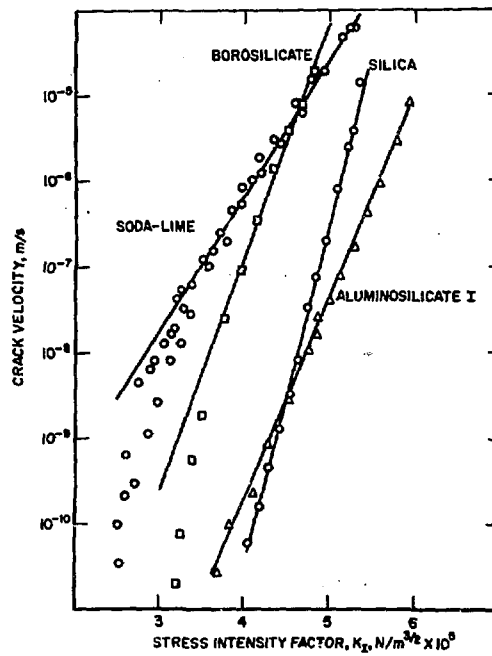


Figure 5. Effect of glass composition on the crack propagation rate in water (16).

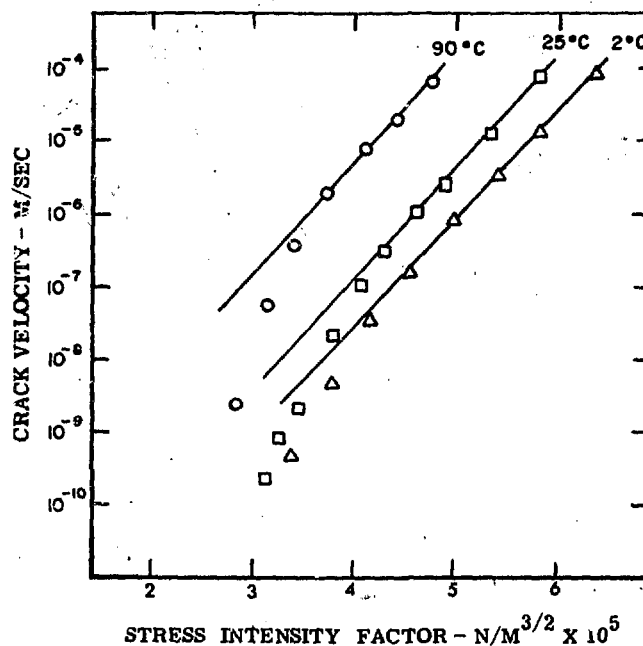


Figure 6. Effect of temperature on the propagation of cracks in soda-lime-silicate glass tested in water (16).

Table 3

SUMMARY OF CRACK VELOCITY DATA
(expressed in the form $v = v_0 \exp[-E + bK_I]/RT$ *)

Glass	E, Kcal/mole, (J/mole)	b, MKS Units	$\ln v_0$
Silica	33.1 ± 1.0 (1.391 E5)	0.216 ± 0.0006	-1.32 ± 0.6
Aluminosilicate I	29.0 ± 0.2 (1.212 E5)	0.138 ± 0.003	5.5 ± 0.4
Aluminosilicate II	30.1 ± 0.6 (1.262 E5)	0.164 ± 0.003	7.9 ± 0.3
Borosilicate	30.8 ± 0.8 (1.288 E5)	0.200 ± 0.005	3.5 ± 0.5
Lead-Alkali	25.2 ± 1.2 (1.056 E5)	0.144 ± 0.006	6.7 ± 0.6
Soda-Lime	26.2 ± 1.1 (1.088 E5)	0.110 ± 0.004	10.3 ± 0.5

measurements, Figure 2. The strong dependence of stress corrosion cracking on composition suggests that this effect will be important for long term durability of the glasses to be used in waste disposal.

Fracture mechanics techniques have also been used to study the effect of temperature on stress corrosion cracking (16). In Figure 6 a study is presented of crack propagation of soda-lime-silicate glass in water, conducted at three different temperatures. At high crack velocities, the crack velocity may be expressed as an exponential function of the applied stress intensity factor, but at lower velocities the data all seems to approach a common static fatigue limit. There is also a temperature shift, so that as the temperature is raised crack propagation occurs more easily. Since this type of data may also be expressed in the form of an activated process, it is consistent with that obtained by Charles who used strength techniques to measure the activation energy. The activation energies of glasses studied to date vary from approximately 25 to 33 Kcal/mol (Table 3). Since fracture of glass occurs more readily as the temperature is increased, the fracture behavior of glasses for waste disposal should be studied at elevated temperatures. The results from such a study should be useful for improving the mechanical reliability of these glasses at temperatures expected during encapsulation and storage.

Crack propagation in glass is strongly influenced by the composition of the crack tip solution and the ion exchange that can occur between that solution and mobile ions that are present in the glass (17). This effect has been studied by both strength (18) and fracture mechanics techniques (17,19). Glasses that have a basic solution at the crack tip (high pH) also have a relatively low sensitivity of crack velocity to applied stress. Conversely, glasses that have an acidic solution (low pH) at the crack tip have relative high resistance to crack propagation. This is illustrated in Figure 7 for silica glass immersed in buffered pH solutions ranging from 1.8 to 12.2. Although straight lines are obtained for each solution the slope of the lines depends on the solution pH. This behavior is caused by ion exchange at the crack

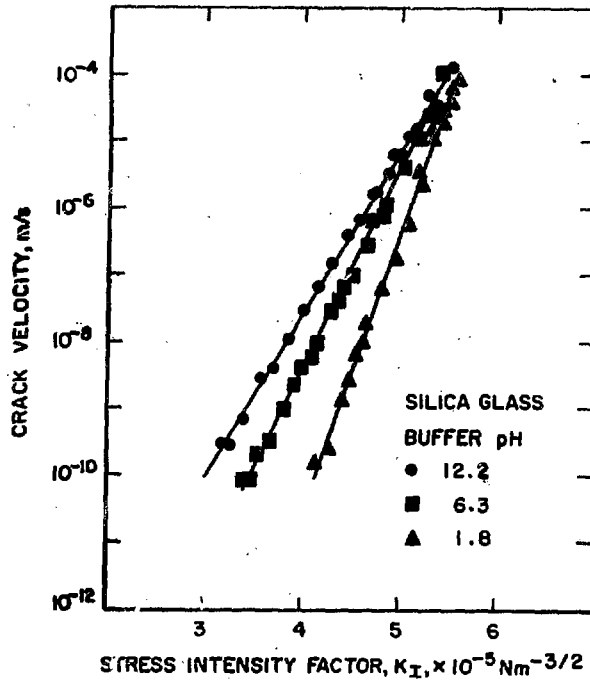


Figure 7. Effect of pH on the propagation of cracks in silica glass, (17).

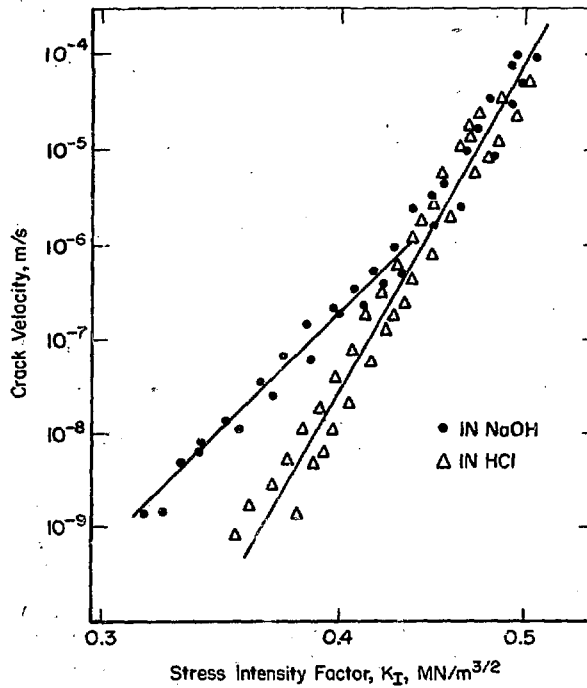


Figure 8. Effect of glass composition on the propagation of cracks in a high silica glass (92.5%SiO₂, 7.5% TiO₂) tested in 1 N HCl and 1 N NaOH, (19).

tip. When crack propagation occurs in an aqueous environment, mobile ions in the glass exchange with ions in the crack tip solution, to produce a solution at the crack tip that differs from the bulk solution. This effect is demonstrated in Figure 8 which presents crack propagation data on a high silica glass (92.5% SiO_2 , 7.5% TiO_2) (19). In 1 N HCL a single curve is obtained which is identical to that obtained in water. By contrast, in 1 N NaOH the data can be represented by two curves. At low velocities the slope of the curve is about one-half that obtained in HCL, while at high velocities the slope is the same as that obtained in HCL. Apparently, ion migration from the glass modified the solution so that it became acidic at relatively high propagation rates. Other data support the dominant role of ion exchange in controlling the crack propagation rates, (17). This effect may be important in waste glasses, which contain mobile alkali ions. These ions will result in a basic crack tip environment that will enhance the rate of crack propagation in these glasses.

APPLICATION OF FRACTURE DATA FOR DESIGN

Strength and Fracture mechanics data can be used for two purposes: to select glass compositions that will be most resistant to fracture for a given application; and to predict the time-to-failure, or the fracture strength of glass under a particular set of loading conditions (20-26). In recent years a well developed design methodology that is based on fracture mechanics has been evolved for these two applications. The details of this methodology are briefly outlined here. For either of these applications two types of information are needed: the fatigue properties of the glasses must be characterized, and an estimate must be obtained of the maximum size flaw that is present in the glass. Fatigue can be characterized by three techniques: by dynamic fatigue measurements; by static fatigue measurements; or by fracture mechanics techniques. The flaw size can be also obtained by three techniques: by nondestructive evaluation; by proof testing; or by statistical analysis of strength data.

Once the fatigue properties have been characterized and an estimate of the flaw size has been obtained, it is possible to determine the rate at which a crack will

grow when glass is subjected to load. The rate of crack growth can be determined for both static and dynamic stress fields, and once the crack growth rate has been determined, an estimate can be obtained of the time required for the crack to reach a critical size for failure. Thus, the failure time and the strength can be obtained from fundamental fracture data. This approach to fracture has been used to determine proof test levels for the glass panes in both the Space Shuttle and the Skylab Space Vehicles. It is also being used to screen glass optical fibers for tele-communication purposes, and to predict weakening that occurs when glasses and ceramics are subjected to thermal shock (27,28).

Glass for nuclear waste disposal will also require a sophisticated approach to prevent fracture in service. The most practical experimental approach to the problem will probably combine statistics (to estimate the initial flaw size) with strength techniques (to determine the fatigue behavior of the glass). From a finite element analysis (or some other elastic analysis technique) the time dependence of stress within the glass can be determined. When combined with information on the flaw size and the fatigue properties of glass, this information can be used to determine the conditions for fracture and the amount of fragmentation after fracture has initiated. This approach was used by Hasselman to estimate the amount of fracture that occurs during thermal cycling of glass (27,28) and is found to agree with experimental measurement. An approach of this type would be ideally suited for application to waste glasses.

SUMMARY

In this paper the fracture of glass has been reviewed and related to problems of waste disposal. Many of the techniques that have been developed to improve the reliability of structural glasses will be applicable to glasses intended for radioactive waste disposal. However, there is a little information on glasses intended for waste disposal. Since these glasses have a much lower silicate content than the usual commercial glasses their mechanical properties may differ significantly from

those of commercial glasses. Therefore, one area of need is to characterize the mechanical properties of glasses intended for waste disposal. The mechanical behavior of these glasses should be determined in both dry and moist environments.

Another area to be studied is that of radiation damage, and its affect on mechanical properties, since no data of this type can be found in the literature. Glasses to be used for waste disposal should be damaged by either neutron or gamma radiation, and their fracture properties should be determined. Information of this type should supplement that obtained as a function of glass composition, and should permit a more definite analysis of the expected lifetime of these glasses in service.

Finally, an investigation should be conducted to determine the effect of second phase formation on the strength of glass. Because much of the literature on the fracture of ceramic materials is concerned with relatively homogeneous glasses or on fully crystallized ceramic materials, there is very little information on glasses that have been phase separated or crystallized. If glass ceramics are used for waste disposal, this type of information will enable us to estimate the amount of fracture after encapsulation. The information can also be used to estimate the effect of the initial stages of phase separation or crystallization on the fracture properties of otherwise homogeneous glasses.

In summary, while a great deal is known about the fracture of glass there is little that is known about the fracture of glasses that will be used in waste disposal, or how the conditions of waste disposal affect fracture. Information of this type, which can be obtained with existing techniques, will be of value for improving the reliability of the glasses to be used for the disposal of radioactive wastes.

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GROUP REPORTS
ON THE BEHAVIOR
OF GLASS AND CRYSTALLINE CERAMICS
AS WASTE FORMS

LEACHING OF GLASS AND CERAMIC WASTE FORMS

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GROUP FINDINGS

The consensus of the committee is that there is relatively little basic science data available to predict the long term leaching of glass, glass-ceramic or ceramic waste forms. A systematic investigation of the influence of the severe environmental conditions expected in nuclear waste storage on the leaching of a variety of simple and complex glass compositions with and without controlled crystallization and polycrystalline ceramics of equivalent composition must be done to establish a scientific basis for long term predictive capability. Of particular concern is the lack of information on the effect of water at high pressure and temperature, the influence of water contaminated by radiolysis and waste reaction products, the effects of transmutation and density changes, the relative importance of grain boundaries, grain boundary phases and porosities of polycrystalline ceramics and the effects of phase separation and microstructure on the leaching of glass and glass-ceramics. There is also considerable concern about the lack of standard tests that reflect valid leaching acceleration conditions and cover the wide range of pH, temperature and pressures that may be encountered in the storage environment.

SPECIFIC QUESTIONS

A series of twelve questions were discussed by the committee. Although the committee felt that all twelve questions were important to the understanding and control of the leaching of glass and ceramic waste forms, a relative priority of importance was discussed. The questions that follow and the discussion thereof are presented in the relative order of importance established by the committee. It is important to point out that no fine distinction between the relative order was present in the committee's evaluation.

1. What are the Effects of Radiation on Leaching?

Studies conducted at PNL and Savannah River Laboratories show no large effect of in situ radiation on the leaching of the waste glass compositions studies. This is most encouraging. However, it has been shown, as reviewed by Primak in this workshop, that radiation tracks on silicate glasses lead to faster leaching rates. Also, a study by Rauscher and Tischer (Proc. 7th. Int. Congr. on Glass, Vol. 2, paper 3030, 1965) has shown enhanced solubility of neutron-irradiated borosilicate glasses. Consequently, it is uncertain at this time whether or not there is a significant compositional dependence on radiation enhanced leaching of glass. It is also unknown as to whether there is a significant effect of the type of radiation or duration of radiation on the leaching of glass. Consensus of the committee is that prediction of the effects of composition or type and duration of radiation on leaching is not likely with the present state of knowledge. It is possible that improvements in intrinsic leach resistance of glasses may be offset with increased sensitivity to irradiation enhanced solubility. Selective leaching mechanisms may be less sensitive than uniform dissolution to irradiation. Further work is needed to establish this point.

Transmutation effects are probably both important for glass, glass-ceramic and ceramic waste forms. The density changes accompanying transmutation effects are likely

to be significant in altering the leaching rates. Redox reactions resulting from radiation damage may also affect both surface and bulk leaching rates.

The consensus of the committee is that polycrystalline materials are likely to be more dependent on radiation than glassy waste forms. The effect of crystallinity on radiation enhanced leaching might be investigated by comparing the leaching sensitivity of metamict minerals with minerals of similar composition that are polycrystalline. It is also agreed that a scientific investigation of the leaching behavior of polycrystalline ceramic, glass-ceramic, and glasses of the same composition exposed to various radiation environments followed by leaching tests is necessary to answer this question fully.

Of considerable concern is whether radiation alters the pH and eH of the water. Is water containing radiolytically produced by-products more reactive with a glass on ceramic surface than pure water? No data are available to answer this question at the present time.

2. Can the Waste Form Composition be Tailored to Minimize Leaching or Loss of Radioactive Products Regardless of the Phase State of the Material?

The committee feels that the answer to this question is definitely "Yes." The review of the compositional studies of the PNL glass waste form program by Mendel, et al., the review of general glass compositional additives by Hench, and the review of the compositional modifications of polycrystalline ceramics by McCarthy establish strong documentation that compositional tailoring can be done in either glass, glass-ceramic, or polycrystalline ceramic materials. Therefore, it is the conclusion of this committee that research to establish optimal compositional modification of waste forms may be expected to yield a high payoff in decreasing the net loss of radioactive products under conditions of leaching.

3. Is Water Composition in Terms of Activities of Mobile Species, pH, and Pressure Important?

This is an exceptionally important variable with very little scientific information from which to establish its relative importance on leaching of either glass or ceramic waste forms. The following environmental variables must be systematically understood: water composition in terms of activity of various mobile species, particularly alkali and transition or rare earth elements; temperature; time; pH; pressure; redox potential; oxygen fugacity; eH; the surface area to solution volume ratio; flushing or replenishment rate of the attacking solution; radiation type, intensity and duration.

In addition the committee feels that the following materials variables are important in understanding the leaching of both glass and ceramic waste forms: composition; volume fraction of second and third phases; porosity; microstructure in general; homogeneity; strain; and rate of new surface generation.

4. What are Valid Accelerated Leaching Tests?

No well established accelerated leaching tests are presently available. Hench's review of recent studies shows that attempts to accelerate leaching by using high temperature autoclave conditions alters the sequence of surface reactions that occur on glass samples. Consequently, an investigation must be conducted to establish valid means for careful extrapolation of data over the 25°-95°C regime to long periods of time.

5. Can a Standard Leaching Test be Adopted?

It is concluded that establishing standardized tests is extremely important. The standard tests must serve at least the following purposes. First, a test should make possible reproducible comparison of materials between various laboratories.

Secondly, a test must be established which makes it possible to extrapolate leaching data to very long time regimes. In order to make such extrapolations valid a test must be designed to examine the effects of low and high pH, high temperature and pressure conditions, variations in temperature and representative environmental solutions. Replenishment and flushing of solutions must also be examined. The test must be sensitive to preferential leaching and cyclic behavior of test solutions and temperatures.

Of prime importance, a standard test must be designed and accepted by the scientific community so that fundamental kinetic and steady state data can be obtained to establish a scientific basis of extrapolation to long time regimes.

Standard tests must also be designed to model appropriately the types of complex geometry and environmental conditions that may be expected in long term storage.

6. Are Leaching Kinetics and Mechanisms (Time, Temperature Effects) Understood?

There is unanimous agreement by the committee that the answer to this question is "No" with the exception of some very simple alkali silicate, model glass systems over a very limited range of temperature and times. The effects of transition and rare earth elements on the leaching of glasses and ceramic materials in a hydrothermal environment are not understood at all. The possibility that such elements may produce unknown redox effects at the surface of the material which could lead to serious alteration of leaching rates is of great concern. The influence of transmutations such as cesium transmuting to barium has not previously been considered. The influence of pressure on the kinetics of glass ceramic surface reactions is an unknown area of research.

7. What are the Similarities/Differences Between Leaching of Glass and Ceramic Materials?

Unanimous agreement exists that little data is available to compare in a scientific manner the leaching rates of ceramic polycrystalline materials with glasses of

equivalent composition. Natural minerals that have shown resistance to leaching during geologic times and polycrystalline ceramics of an equivalent composition should be studied. Glasses of the same composition should be prepared and investigated. Comparison of leaching mechanisms and rates for such systems should provide a strong scientific basis for understanding the different types of materials.

German investigations of glass ceramic waste forms may provide a data base for comparing glass-ceramic and glass materials for equivalent composition.

Comparison of archeology data on ceramics and glasses that have been exposed to the biosphere for long periods of time may also provide data as to reaction mechanisms and kinetics, if the dating is well established. Likewise, data on weathering of feldspars and clays and the dissolution of quartz from geochemical studies can provide an important data base for understanding the long term leaching of both glass and ceramic waste forms. Dating of volcanic ashes via devitrification techniques and rates of soil formation from volcanic origins in Hawaii may also be valid sources of information in making these comparisons. Selective leaching of volcanic deposits may provide information as to the type of preferential attack of glass waste forms. The genesis of ore deposits and origin of polycrystalline materials that exist within the ores may also be an important source of information.

It is recommended that a research task force of interdisciplinary nature involving geochemists, glass and ceramic scientists and waste management personnel be created to evaluate systematically the existing literature in the areas described above in order to establish a comprehensive basis for comparing the leaching and weathering of ceramic and glassy materials over short to geologic time regimes.

8. What are the Effects of Phase Separation and Microstructure on the Leaching of Glass and Glass-Ceramics?

In the commercial soda-boro-silicate glasses the effects of phase separation on leaching is well understood. However, only a small area of the soda-boro-silicate

system has been extensively investigated, particularly the compositional regime that includes Pyrex^(R) Brand Code 7740 glass and the base glass for VYCOR^(R) Brand commercial glasses.

It is important to investigate a wide range of glass compositional systems to determine the effects of volume fraction, connectivity, and composition of phase separated regions on leaching rates and mechanisms.

Phase equilibria diagrams should be related to glass formation regions in the same compositional binary and ternary diagrams and the effects of varying the type and volume fraction of different crystal phases on leaching be determined. Thus, the effects of either controlled nucleation and crystallization or uncontrolled devitrification on the rates of leaching can be related back to the phase equilibrium literature that already exists.

9. Is Leaching Behavior Related to the Mechanical Properties and Fracture of Glasses?

Weiderhorn's review establishes firmly that stress corrosion effects are extremely important in the fracture of glass. There is considerable concern that the increase in surface area of the glass due to fracture during processing and while in storage may significantly alter leaching behavior. Since local solution pH can be significantly increased by increasing the surface area of glass exposed to the leaching solution it is important to understand the influence of formation of new fracture surface area on leaching rates. Fracture mechanics can be used to calculate the fracture of the glass into equilibrium sized granules assuming the temperature profiles to be encountered in the casting process. The change in the surface area with time due to progressive fracture can also be approximated by such mechanics calculations. Relating the surface area and change in surface area with time to leach rates can and should be done experimentally in a research program.

^(R) Corning Glass Works

10. Can Compositional Additives be Designed which will Minimize Leaching?

The review on leaching of glass by Hench summarizes findings that additions of various ions added to corrosive solutions can serve to passivate the surface of glass to further leaching. Consequently, it seems quite likely that tailor-made compositional additives can be designed which can be added to the waste form canister after the glass has been cast or to the storage site. Such powders would be preferentially dissolved by any penetration of water to the canister or storage site and the solutions would percolate through the granules of the glass. Passivation of the glass surface by the percolating additive ions can be expected. Such a concept would be quite compatible with the existing glass casting processes being considered and research in this area is recommended.

11. What are the Most Severe Conditions Encountered in Leaching?

The environmental conditions associated with salt mines, shales, basalts, and granites that are considered for long term storage of the canister should be summarized in a short report and made available to the materials science community. These conditions should be well known by the investigators of glass and ceramic leaching so that modeling experiments can be designed. The influence of salt brines on the leaching of glasses is generally not understood. Effects of pressures as high as 2500 psi due to underground storage is also not understood. The possibility that pH may significantly increase under pressure in certain deposits is a serious concern since high pH produces rapid attack of silicate glasses.

12. In Crystalline Materials, What are the Effects of Grain Size, Grain Boundary Phases, and Stoichiometry Changes on Leaching?

Little or no systematic investigation of these variables has been conducted. Basic research on these variables is essential if leaching of ceramic waste forms is to be understood.

RADIATION EFFECTS

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This group addressed itself to three questions aimed at (1) defining the sources of radiation which must be considered; (2) the effects of irradiation on materials Properties; and (3) recommendations for research in this important area. The specific questions and a summary of the discussion follows:

1. What are the most important aspects of radiation damage which influence the stability of nuclear waste forms over short-term and long-term storage? (The difference between short- and long-term storage is arbitrarily defined as ca. 500 years.)

It was concluded that, based on calculations previously made, the neutron fluence resulting from spontaneous fission and from (α ,n) reactions is comparatively low and that neutron damage to nuclear waste forms will probably not be a major effect. The high concentration of relatively short-lived beta emitting isotopes suggest that this will be a major radiation damage concern over the short term.

Though the displacement effects resulting from beta irradiation are comparatively small in those materials not subject to ionization damage, transmutation is a major concern due to alterations in ionic charge and size and needs to be studied. The effect of alpha particle irradiation and its associated heavy daughter recoil are of concern over both short- and long-term storage due to the large number of

displacements generated per event. For some crystals this may lead to total disorder, i.e., the metamict state.

Calculations indicate that, for a reference high level waste from spent LWR fuel, about 0.1 and 1 dpa are expected from alpha decay after 10^3 and 10^6 years storage, respectively, which is small compared to the projected damage in metallic components in LMFBR and CTR systems. The corresponding helium concentrations are about 100 and 1000 appm, respectively. The above calculation assumes, however, that the actinides are homogeneously dispersed and the damage could be much more severe if segregation were to occur or if waste loadings are increased above the concentration presently anticipated. The same pertains to the helium generated and it was concluded that helium effects may be more of a long-term problem in crystalline forms than in glass. The role of ionization damage in glasses and ceramics is difficult to predict; in some materials the effects may be important from the standpoint of bond disruption, valence change, and atomic displacements. Radiolytic processes, such as decomposition, must be considered not only in the waste form and its canister, but also in the interaction between waste and the geologic disposal media. The effect of moisture needs to be taken into account in radiolysis.

2. What are the effects of irradiation considered in question 1 on crystalline and glass waste forms?

In assessing irradiation effects on materials behavior, it was concluded that more precise information is needed on the radial time-temperature profile in the waste form. In heat transfer analysis, it is necessary to consider varying degrees of cracking of the waste material, the formation of gaps, interaction between the waste form and canister, and heat dissipation characteristics of the surrounding geologic media. Volume changes are likely to be the most important macroscopic radiation damage effect and could result in cracking, reduced thermal conductivity,

increased chemical attack between the waste and canister, and increased leachability. Thermal conductivity can also be affected by radiation induced microstructural changes. The extent of stress-induced cracking will depend on homogeneity and initial strength of the waste form and the magnitude of the volume change incurred. It is reasonably well established that the maximum volume change in alpha-recoil damaged glass is <2% whereas a number of crystalline materials are known to undergo larger volume changes of up to 15-20%, if they approach the metamict state. If metamictization does not occur, swelling of ceramics can be quite small (<1%), but little is known about the radiation stability of the phases present in current crystalline waste forms. In view of these considerations, homogeneous glasses are expected to exhibit smaller radiation damage effects than multi-phase crystalline waste forms.

For glass it is necessary to identify the extent of homogeneity and under what conditions crystal formation occurs, and for all waste forms the precise phase composition and stability of the phases formed must be determined. The effects of transmutation on the stability and reactivity of glasses and crystals is a large unknown, but is likely a larger problem in crystals than in glass. Other important variables which should be considered include time and temperature (annealing), total dose and dose rate, structural features such as sinks and crystal size in ceramics and devitrified glass, and the presence of helium, particularly when concentrated so that localized high internal pressures are generated. Radiation may also influence properties such as devitrification, phase transformation, leachability, thermal conductivity, and mechanical properties.

3. What work is needed to provide the necessary understanding of short- and long-term radiation effects on nuclear waste forms?

The general area of phase behavior studies to define the extent of homogeneity in glasses, the composition and conditions of formation of devitrification products,

and the effect of self-irradiation in devitrification behavior is needed. Simultaneously, efforts need to be directed toward defining the phase location of each radionuclide in crystalline materials and glass ceramics. Studies of this type are needed to determine the degree to which radiation damage may be localized. The process of metamictization needs to be studied further and the mechanism(s) by which certain crystals and natural minerals amorphize or glasses alter their structure should be investigated to better define long-term order/disorder phenomena in glass and crystals.

Since the radiation effects considered in the storage of nuclear waste are long-term (compared to laboratory-scale experiments), accelerated tests involving damage simulation are necessary. Doping studies using short-lived actinide isotopes such as curium-244 should be continued to allow simulation of thousands of years of storage in a few months. This type of study allows both displacement and helium effects to be observed. Ion beam irradiation using protons, alpha particles, and heavy ions allows radiation damage to accumulate even faster and can be used to study the approach to metamictization, gas buildup, devitrification, and dose rate effects to damage levels beyond 10^6 years. However, the effects of accelerated testing on the accuracy of damage simulation must be considered. Neutron induced transmutation, gamma-ray irradiations, and electron irradiations are necessary to obtain the complete picture. In addition, modeling studies need to be conducted to describe the radiation, thermal, chemical, and mechanical behavior of nuclear waste forms over their projected storage life.

Fundamental radiation damage studies on model systems such as MgO , Al_2O_3 , simple glasses, and simple crystalline silicates will aid our understanding of radiation effects in multicomponent, complex nuclear waste forms. The processes to be studied include damage mechanisms, type and rate of defect formation, defect agglomeration, i.e., cluster formation, annealing (recovery) behavior, and radiation

enhanced diffusion. The effects of irradiation on properties such as leaching, stored energy, thermal conductivity, dimensional changes, creep strength, and fracture behavior should be studied in these model compounds. The understanding obtained in these studies on simple systems would provide valuable insight to the question of radiation stability of complex, multicomponent nuclear waste forms.

THERMAL EFFECTS

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Radioactive decay causes nuclear wastes to behave as if a uniform heat source were distributed within the material. Naturally, the intensity of the source, which is proportional to the fraction of active material in the waste, decays slowly, being nearly inversely proportional to time. In the absence of convection within the waste form, a uniform source causes a slab, cylinder, or spherical shape to adopt a temperature distribution which is parabolic. The temperature differential between centerline and surface is directly proportional to the source intensity and to the square of the characteristic dimension, and inversely proportional to the thermal conductivity of the material. The difference between the surface temperature of the waste form and the ambient temperature is directly proportional to a characteristic specimen thickness, and inversely proportional to the surface heat transfer coefficient. Thus, the center or maximum temperature of the waste form depends on all these factors.

The thermal conductivity of the glass waste form is sufficiently well known. Because of the low thermal conductivity of glass and the relatively small crack density of thermally-shocked canisters, the diminution of the effective thermal

conductivity is insignificant on fracture. Polycrystalline ceramics typically have conductivities which are slightly higher than glass and easily determined.

The effective heat transfer coefficients between the canisters of radioactive waste and their geologic environment are being determined (Oak Ridge) and that calculations on the long-time temperature distributions in storage are underway. Freedom to choose the characteristic dimension allows temperature distributions (as a function of time and position) to be selected from a variety of possibilities. There are opposing effects arising from temperature considerations. Higher temperatures give higher defect annealing rates and higher helium permeability (which seem desirable) and higher phase separation and leaching rates (which seem undesirable). Thus, there is a likelihood of an optimum temperature distribution. Surface temperature has probably the most direct effect because the rate of leaching or dissolution of the waste forms are strongly dependent on this temperature. It is important to emphasize that interface temperatures will be higher than ambient temperature and this must be taken into account. Further, the temperature difference between the waste form and the ambient (brine, water, humid vapor, etc.) will cause thermal convection in the ambient that may enhance the leaching or dissolution rates.

Thermally-activated phase separation processes can affect the homogeneity of the radiation damage, the kinetics and mechanisms of leaching, the kinetics of evaporation, and the nature of waste/host rock interactions. For a glassy waste form, the important phase separation processes are crystal precipitation and growth, sometimes called devitrification, liquid-liquid immiscibility, helium precipitation as bubbles, and finally volatilization. Several of the alternative (crystalline ceramic) waste forms approach thermodynamic and/or kinetic stability over the waste storage temperature range, so the first two types of phase separation do not apply.

However, it cannot be certain that they will likewise be stable to the varying radiation field which they will experience. Crystalline waste forms can be prepared to have varying amounts of well distributed porosity which can provide sites for He collection.

Devitrification rates at constant temperature are typically constant functions of time. Thus, to extrapolate from a week's experiment crystal sizes of 50 μm in 1000 years requires the ability to measure growth of 1 nm. This seems to be several orders of magnitude lower than can be measured by classical means. Thus, extrapolation from higher temperatures is presently the best available means of predicting the long-term behavior. Clearly, the longer the time and the lower the temperature of the experiment, the greater the certainty of extrapolation.

It is fortunate that precipitation processes, even in multicomponent glass-forming systems, are relatively well understood on a fundamental basis, especially since heterogeneous nucleation on the impurities is probably quite easy, in particular on the undissolved Pd, RuO_2 , CeO_2 , and ZrO_2 particles of the waste form. The major problem here, in common with other thermal effects, is how to reliably extrapolate results to low temperatures. Well below the liquidus, the temperature dependence of the precipitation kinetics of a species which is of different composition from the bulk is determined by the temperature dependence of the interdiffusion coefficient matrix. This dependence introduces two complications for reliable extrapolation. First, the individual elements of the interdiffusion matrix may have different temperature dependencies. Second, the form of the temperature dependence of each of these elements can be expected to change at the glass transition temperature. Since the temperature dependence of transport coefficients is smaller below the glass transition, extrapolation from above to below the glass transition might give unrealistically low rates. A more conservative prediction would use only half the measured activation energy in extrapolating from the glass transition to lower temperatures.

To achieve greater certainty, year-long annealing times below the glass transition will be required and are being conducted. Crystal sizes will probably have to be measured by transmission electron microscopy or inferred from light or small angle x-ray scattering patterns. The similar set of circumstances for liquid-liquid immiscibility suggests that these same techniques will be most appropriate for study of liquid-liquid phase separation kinetics at temperatures below the glass transition.

Helium penetration studies can be made provided that thin enough layers of glass can be produced to allow permeation within reasonable times. These can yield both diffusion and solubility information. Such measurements are recommended and are already underway. To date, experiments with markedly higher than normal curium impurity (so as to simulate in a shorter time the α production equivalent to that obtained in long-time storage) have not caused observable fracture or fragmentation of simulated waste glass composition, although helium ion-implantation studies have revealed fragmentation of low permeation glasses. The expected radically lower solubility and diffusivity of He in crystalline waste forms and the current lack of any experiments in crystalline waste forms suggest that such measurements are vital at present to aid in the comparative evaluation of crystalline and glassy waste forms.

Identification of the crystal phases in which the actinides are concentrated is surely the first step, since α particles are typically of quite short range and the radiation damage they produce should be limited predominantly to the phases containing the actinides. It may turn out that the small grain sizes and porosity in the polycrystalline ceramics could allow even the complete disintegration of the relatively small volume fraction of actinide-containing phases without significant degradation of the integrity of the composite. If adverse He effects were found, more desirable crystalline host phases for these actinides could be sought. Although additional processing costs would be required to produce the multi-barrier waste form, the tough coatings used on supercalcline cores in this scheme should insure the integrity of the pellets in spite of He generation effects.

Initial transpiration studies of evaporation kinetics of various species from a simulated waste form glass have recently been completed. They provide the basis for estimation of volatilization kinetics at lower temperatures. The difficulties with extrapolation to below the glass transition mentioned earlier still apply because one expects that ΔH_{vap} will be lower beneath the glass transition. The results indicate, however, that extrapolation to the glass transition alone will result in very low evaporation rates for Cs, the most volatile species even under the worst condition. Nonetheless, it is deemed important to determine for species of high activity such as Cs the fundamental parameters that affect the volatilization kinetics: vapor pressure, diffusion coefficient, and surface reaction rate at sufficiently different temperatures to permit extrapolation. These factors are important for any composition considered for long-time storage.

Even if waste forms interact with the geologic environment by dissolving or being leached, it is possible that the reactions will produce stable immobile compounds. Thus, it seems essential to determine what the stable phase assemblages will be when various waste forms equilibrate with a given quantity of their "geologic environment".

As surely pointed out in the radiation damage section, the production and annealing of radiation defects in various waste forms are important since both solubility and leach rates can be affected by radiation damage. (Results to date show little sensitivity of leach rates of glasses to radiation damage.)

Although present large-scale simulated thermal shock tests have indicated no serious pulverization of the glassy waste form by thermal shock, it is deemed advisable to calculate and confirm with measurements the magnitude of residual stresses that will be produced in waste glass forms. The results will not be equivalent to those obtained in ordinary inactive glass forms because of the effect of self-heating. Also required are estimates of the residual stresses produced by

precipitation of various phases for temperature distribution both above and below the glass transition temperature. Information regarding thermal expansion and molar volume both below and above the glass transition, for the glass and all phases that may be produced, is necessary to obtain numerical estimates of the residual stresses. The anticipated stress distributions from cooling and from phase transitions will be functions of time, position, and size of the waste form. They should allow fracture mechanics to be applied to potential pulverization of the waste form.

A system maintained with a non-uniform temperature distribution for a long period will tend to become chemically inhomogeneous. This process, called thermal diffusion, deserves study in waste glass systems because it is a type of separation within a single phase that diminishes homogeneity and affects leachability and dissolution kinetics.

The large amount of information gathered during empirical development of waste glass compositions both here and abroad deserve synthesis and summary. A unified viewpoint regarding the composition-property relationships, including consideration of the composition regions which readily form glass, would be helpful to the waste program and to glass technology generally. If it is possible to simplify complicated compositions, e.g., by grouping oxides into classes and thereby generating (say) five or six component systems that have essentially equivalent properties to the waste glasses, then equilibrium phase information would be most useful in evolving an optimum composition. It almost seems axiomatic to state that the more levels on which we can understand the waste form, its structure, and thermal properties, the greater the probability that all aspects of its future behavior can be anticipated.

Thus far, many full scale and smaller simulated experiments have been conducted on waste glass forms; these given confidence that the glassy waste form is suitable under short-term conditions and no obvious long-time difficulties are apparent. It

is the subcommittee's belief that there is merit in pursuing concurrently the suggestions made in this report in actual waste glass systems, in model glass systems containing a smaller number of components in dense polycrystalline ceramics, and in composites.

LONG-TERM STABILITY OF CERAMIC RADIOACTIVE WASTE FORMS

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INTRODUCTION

Initial discussion in this group started with an effort to identify the specific long-term stability criteria which should be met by a suitable waste form for high level wastes. There was considerable concern about a lack of knowledge of the long term leaching properties of the proposed waste forms which will impede selection and placement in a repository with sufficient certainty that none of the dangerous elemental species in the waste would enter the biosphere. Achievement of this objective is very difficult since many critical waste-form properties have not yet been identified or measured, and the geologic conditions for waste storage are uncertain since they are dependent on the repository site and a number of these are still being evaluated. In this text, the term "ceramic" is used to include both glass based and the more crystalline candidate waste form materials. Due to the uncertainty for specific waste form criteria cited above, further discussion was focused on the following matters.

DISCUSSION TOPICS

1. Leaching of selected radionuclides from a candidate waste form material to relevant times was felt to be the most important criterion by which the proposed materials should ultimately be evaluated. This immediately led to the question as to how leaching properties of waste forms can be determined for various ceramic

candidate materials in realistic experimental times so as to be sufficiently complete that the data can be adequately understood and the extrapolations be defended and have meaning for periods of 1000 to perhaps a million years into the future. A view was expressed that (1) glass-based waste forms will tend to be more stable than polycrystalline polyphase forms during the long times of interest, and (2) that there is more promise in the near term for understanding the prospective long term behavior of a glass-based waste form than for the less studied crystalline forms. Within the discussion group there was disagreement over item (1) and a majority opinion on item (2). It was stated that the relative lack of radiation damage information on crystalline waste forms was due to less work which has been done on this type of material and that crystalline waste forms can ultimately be understood as well or better than the glass type if sufficient work were done very soon. The observation was made that radiation would make the crystalline form less stable, but less crystalline, while it would at the same time make a glass form more stable.

2. The discussion focus then changed to the subject of the devitrification of glass-based waste forms and the bearing this may have on the long-term stability and usefulness of glasses for this purpose. Little is apparently known concerning the devitrification characteristics of the present candidate waste glasses in the radiation and local environments to be expected in a waste repository once the metal canning material has been removed via oxidation or corrosion. The chemical environments anticipated for the waste form when it is placed in selected geologic formations and the anticipated effects on devitrification of the glass matrix are poorly understood, if at all. Some discussion ensued of the advantages and disadvantages of damp salt vs shale for storage of a waste form. It was pointed out that salt beds may contain water and that this should be more widely recognized and that shales vary widely in chemistry and these should not be considered as simple homogeneous formations in regard to the compatibility of candidate waste forms with these formations. Current work on leaching of glass-based waste forms considers to a

very limited extent if at all such variables as pH and/or ionic environment and oxidation potential anticipated in the geologic formation. It was not apparent that a significant amount of work on leaching and corrosion of the more crystalline ceramic waste forms in these environments is being done at all.

3. Discussion was then directed to experimental designs that are suitable for evaluation of candidate ceramic waste forms, and ultimate demonstration of the viability of a waste form. It was commented that (1) any experiment for this purpose must be performed under conditions where the reaction kinetics are relatively fast so that data can be obtained in reasonable times for use in extrapolations to the very long times of interest and (2) one must be able to measure diffusivities of the relevant species under the proper simulative conditions. Item (2) can be very significant for estimation of crystallization or crystal growth rates of glasses. It was pointed out that although crystallization rates in the glass waste forms are being studied, diffusion measurements have not been included. It was not apparent that sufficient work in this area is being done on any candidate waste form. There were comments on use of predictive equations for leaching processes of commercial glasses and that these equations apply over a very limited range of temperatures. It was felt that sufficient understanding of simulant waste glasses of interest could be obtained in a reasonable time with application of intense effort in the near term. Less certainty was possible for time estimates for experiments on actual radioactive waste glasses. One individual felt that it was quite important that proper distinction be made between studies aimed at understanding devitrification of glasses and those aimed at dissolution of certain species from glasses followed by recrystallization of phases containing these species. Some individuals felt that the radioactivity characteristics of the waste glass would tend to reduce the tendency for devitrification at least during the time period when the major radiation damage was accumulated. However, radiation damage may cause the glass to convert to a different glassy state.

4. Simulating long term radiation damage in the waste form was discussed next. The present state of knowledge on radiation damage mechanisms in ceramic materials was reviewed, indicating that damage in both ceramics and glasses is complex and not well understood fundamentally at this time. The only means described for artificially doping a simulant glass for study of radiation damage and its relation to long term stability of the waste form employs ^{244}Cm additions. The principal damage mechanism being simulated is α recoil damage. Questions were raised concerning the basis of the assumption that ^{244}Cm decay would adequately simulate the radiation damage imparted to an actual waste glass because of assumptions concerning damage rate effects and the basis for extrapolations of these damage effects to the long times of interest for actual waste glass. One point of concern expressed was whether the ^{244}Cm will have the equivalent spatial distribution in the simulant as the actinides will in the actual waste glass. If it does not, the ^{244}Cm additives may not adequately simulate the radiation damage conditions in the actual waste glass. Very little radiation damage studies using other techniques such as neutron as ion simulation are currently being done on the candidate crystalline waste form materials.

5. Up to this point in the discussion, most of the attention had been focused on glass-based waste forms. The discussion was then diverted to the more crystalline or so-called ceramic waste forms. Comments were presented supporting the view that these crystalline or poly-phase waste forms offered considerable promise for use in lieu of the glasses discussed previously, but that there has been insufficient investigation of these alternative materials. There was discussion without agreement, on the possibility of heterogeneous leaching and radiation damage in the crystalline forms making them less attractive than non-devitrifying glasses. While glasses are not major geologic species, it was pointed out that natural glasses do exist with ages $> 10^6$ years. It was a majority opinion however that so much work has been done on glass-based waste fixation processes that very significant efforts would be required

very soon on alternate waste forms and the processes to produce them in order to generate data required for an intelligent comparison of expected performance of the candidates. If funds are limited for waste form development, the consensus of the group was that due to the much greater amount of work which has been done on glass-based waste forms these should probably be favored for near term applications. Due to the importance of this technology to the ultimate future of nuclear power, the group felt that development of at least one waste form alternate to glass should be pursued vigorously. The development of only one generic waste form was felt to be inadequate at this time due to the uncertainties in several properties of all waste form materials. What will be the situation with nuclear power if (1) only the glass-based waste form is developed to production scale and (2) unsatisfactory properties such as high leachability appear for the actual waste glass some years following its introduction to a repository?

6. There was a comment that radiolysis effects on any water present in the environment of the waste form during storage may have a very strong effect on glass-based waste forms and probably on the more crystalline type of waste forms as well. In this regard, it was pointed out that since the more crystalline waste form will obviously be segregated on perhaps a somewhat coarser scale than will glass based waste form, the long term stability of the more crystalline waste form will be more difficult to study and interpret in regard to data suitable for extrapolation of leach rates, etc. to the times of interest, i.e., 10^3 to 10^6 years and that this will require critical analysis. It was pointed out that there should be a distinction made between the acceptable stability of a candidate waste form and the thermodynamic stability of the material. The rate of re-equilibration of the waste form with mobile species which may invade the repository will be quite important and is a distinctly different matter than the stability consideration. It was felt that the porosity which will invariably be present in the more crystalline type of waste forms will clearly add to the complexity of understanding behavior of these materials.

SUMMARY

The following items were identified as having "high significance" by this group, regarding long term stability of ceramic radioactive waste forms.

1. Leaching processes operative for the waste forms are of major concern. If a standard is adopted wherein the waste form is to retain specific radionuclides for a specific time into the future, then studies of the mechanisms, kinetics, diffusion, etc. for transport of these nuclides from the waste form to the local environment simulating that anticipated in the repository must be undertaken immediately. It was felt that based on presentations at the meeting, very little is currently known about these processes either for simulant or actual radioactive waste forms.

2. The waste form glasses developed to date are assumed to be relatively homogeneous even though they do contain crystalline phases which either do not dissolve in the base glass or they crystallize from the glass during waste form preparation. Based on this homogeneity assumption, the glasses were generally felt to be "simpler" for consideration as waste forms at this time that the more crystalline forms. Strong partisan viewpoints exist in this area concerning the viability of glass-based waste forms versus crystalline forms and the basis of this difference of viewpoint appeared to be partly historical. Sound technical data supporting either type of waste form is not presently on hand since so little directly pertinent information appears to be known about any of the candidate waste forms. Ceramic waste form evolution has been significantly influenced by radioactive waste process development methodology aimed at process evolution, etc. rather than following the inverse procedure of first identifying the best waste form followed by developing a waste conversion process to produce that waste form.

3. The geologic environment in which the wastes will be stored must receive prime consideration when considering long term waste stability of ceramic waste forms.

4. Present understanding of the corrosion mechanisms of relatively simple

glasses provides some confidence that properly oriented studies of simulant waste glasses and actual radioactive waste glasses could in the near term, i.e., less than 10 years, provide a sound basis for long term extrapolation of the behavior of this waste form. Similarly, the crystalline waste form candidate materials should also be studied in this fashion. Work in this area is minimal at the present time.

5. Radiation damage in all candidate waste forms and its potential effects on reaction and corrosion mechanisms of the waste form in the geologic storage environment should be addressed and investigated vigorously.

6. Phase separation and phase transformation processes must be fully understood in the candidate waste forms so that a realistic data base for long term stability extrapolations can be established.

7. Radioactive waste compositions are currently quite variable and this variation has to date resulted in much of the development of glasses suitable for fixing wastes being concentrated on compositions satisfactory for assimilating rather different wastes. If identification of a reference waste composition is not practical for various reasons at this time, then a rather confusing situation will prevail regarding specific waste form compositions whether they be glass- or crystalline-based ceramics, and this will preclude early identification and development of a single optimized ceramic waste form.

ADDITIONAL COMMENTS

One individual suggested that at a total fixed composition, the free energy of the glass is greater than that of crystalline material of similar composition, and thus the crystal should be more stable than the glass. Effects of surface-free energy for the crystalline form are not applicable since for practical grain sizes in the crystalline waste form the contribution of the surface-free energy to the total free energy will be negligible. Unless it is specifically shown that glass has a special structure which leaches the most harmful components more slowly than the specific ceramic assemblage, the first approximation must be that glass will be less

stable from a strictly thermodynamic viewpoint.

In response to this point, it was noted that the free energy difference between a glass and a crystal of a given fixed composition is not related to the leaching kinetics in an obvious way, and leaching kinetics were identified as one of the major concerns. For example, the highly soluble $(\text{Na,Cs})_2\text{MoO}_4$ and the moderately soluble SrMoO_4 may form by crystallizing. A free energy gain in the system achieved by formation of these crystalline phases from their dilute solution in the glass clearly would have an adverse effect on the relative leachability of this waste form.

It was pointed out that "homogeneous" glasses are often not uniform in composition on a scale of tens to hundreds of angstroms, and this compositional inhomogeneity is a function of bulk composition, thermal history, and other variables, i.e., consideration of the "nanostructure" is quite important when glass is considered for use as a waste form.

Nevertheless, it was felt by some that phase separation at the 50 Å level may be far more desirable than the macro-scale heterogeneity potentially present in some crystalline waste forms.

WASTE FORM, COMPOSITION AND PROCESSING

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INTRODUCTION

Various systems have been proposed for the containment of nuclear waste: for the confinement of the waste form in an engineering system in unspecified geologic formations and/or locations. A common conclusion is that the basic waste form should be a ceramic (either glass or polycrystalline) because of the expected increased resistance to leaching by the geological ground waters in comparison with metallic or polymeric materials. Crystalline waste forms are presumed to be more resistant to leaching because of their greater thermodynamic stability than the glasses. A glass is expected to be more leachable than a single stable crystalline phase of the same composition. However, most complex glasses crystallize into multiple phases, with greater and less leach resistance than the parent glass. Similarly, multiphase polycrystalline waste forms would be expected to exhibit variable leachabilities for the individual phases present. Alteration of either glass or polycrystalline forms by the ground waters will yield presently unspecified products with unknown waste product retention capabilities. However, one of the proposed waste disposal systems would involve the direct injection of a nitrate or other salt solution directly into a suitable geologic

formation. The alternate systems involve the assumption that waste solution will be processed to yield a solid waste form to be contained within a cannister for shipment, intermediate term storage (5-10 years), and internment in a repository, and to provide for recovery of the cannister (at approximately 25 years) to inspect the system and determine conformance with the expected behavior of the system design. Confinement of the waste within the localized geological deposit over thousands of years is the goal of the system to be developed. For any of the proposed systems, the criteria to be considered are:

- the capability to accommodate changes in composition of the waste solutions between high level waste and intermediate level waste and possibly high gadolinium contents;
- the ease and reliability of the process to fabricate the selected waste form;
- the minimization of the dispersability of the waste due to an accident in the short-term during processing, storage, transportation, or short-term transportation to the repository;
- conformance to the provisions for Nuclear Safeguards;
- assurance of resistance to leaching by the geological ground waters;
- minimization of the transport of dissolved waste by percolation with the ground water.

The selection of waste forms and fabrication processes can be reasonably compared for most of the above criteria. However, due to the limited interaction with geologists at this meeting, and lack of information about specific ground water systems, (considered as alternate sites) and lack of a capability to predict hundred to thousand year resistance to leaching by any of the compositions or forms to be considered, we are unable to recommend a single specific form as a final choice. Hence, the development of a number of alternate forms for the generation of basic and engineering data needed to choose among them is required.

The solid waste forms considered include (1) a homogeneous glass; (2) a glass: ceramic (assumed to retain a relatively large volume of glass); (3) a multiphase polycrystalline ceramic (which might include a small amount of glass); (4) multiphase cermets with waste dominantly in the ceramic particulates in a metal matrix; (5) crystalline ceramic beads coated with a leach resistance material.

A metallic matrix is suggested as a matrix material and as the canister. Concrete matrices may be suitable for intermediate level waste.

Process techniques exist to make any of the above waste forms with varying degrees of difficulty in an open laboratory or plant. The relative degrees of difficulty in remote handling are presumed to follow approximately the same order considering the number of process steps and the pieces of machinery, moving parts, and the needs for equipment removal and clean-up. Process comparisons for glasses vs. ceramics, for example, are also dependent upon the peak temperature requirements. Too high a temperature in primary processing would lead to a change in the distribution of the off-gas waste, in addition to the specific gaseous wastes. Thus, volatilization of alkalis, Mo and Tc/oxides and oxidation of ruthenium oxide to RuO_4 (which is volatile at low temperatures) make low process temperatures preferred in order to retain as much of the alkalis and other volatiles in the solid waste form as is possible.

GLASS

Much greater effort has been devoted to the development of glass compositions and processes than to any of the other forms. Continued development of the engineering of the glass waste form must be vigorously supported if the present schedule for demonstration of the engineering system for solid waste disposal is to be met.

The zinc borosilicate glass with high leach resistance ($4 < \text{pH} < 10$) and the capability to contain high levels of waste without serious degradation of the leaching or devitrification characteristics, or of the viscosities desired, is reported elsewhere in this report. It has been presumed, as an objective, that development of the glass

would give a truly homogeneous substance which would then offer a uniform and high leach resistance. For the U.S. designed systems which contain of the order of 30% by weight of oxide wastes, the Pd, Ru, Ce and Zr contents in the waste glass give rise to crystalline Pd (metal), RuO_2 , CeO_2 and ZrO_2 particles which could serve as heterogeneous nucleation centers for devitrification during processing, interim storage, or internment. Hence, these inhomogeneities change the basic assumption regarding the leach resistance of an assumed homogeneous glass. There is a prospect that development of ion-exchange processes may remove the palladium and ruthenium. However, that process is not yet available and would presumably not remove the Ce or Zr. (The Canadian systems involve greater dilution of the waste form [to 1 wt% in glass] to promote the solution of the low solubility waste products, i.e., Pd and Ru although these two may not be soluble even at these dilutions).

Secondly, with respect to glass homogeneity, it was pointed out that most glasses undergo phase separation and variable leachability; phase separation would also lead to segregation of the distribution of radioactive elements that would lead to hot spots and potentially an advanced rate of degradation not now predictable. However, the same problem is envisioned for multiphase polycrystalline composites as well.

Two processes for preparing glasses from the calcined nitrate solution, involving direct melting in the canister or crucible melting and casting in the canister have been under development. Both are attractive because of the few moving parts required for the calcining and casting or melting operations.

POLYCRYSTALLINE CERAMICS

Heterogeneous multiphase polycrystalline ceramics are considered next in order of process complexity; these provide for containment of all the solid waste including alkalis, at higher weight percentages of waste and gadolinium than the glass composition developed to date. Thus, lower system costs could be derived from smaller

volumes to be contained. Processes envisioned include calcination, pelletization and sintering or hot pressing. Either of the latter could be carried out with the addition of a small volume fraction of a liquid phase in order to lower the required process temperature.

By analogy to the microstructures developed for corrosion resistance in steel or glass plant refractories, large grain sizes and low porosities are desired for polycrystalline products. Prototype samples have been prepared with grain sizes ranging from 1-10 microns and with porosity sufficiently low to make the samples impervious (with and without glass additions). These exhibited roughly equivalent leach resistance to some glass compositions from standard tests. The opportunities to develop improved corrosion, thermal stress, thermal shock, and impact resistance of multiphase polycrystalline ceramics exists. It has been found that multiply cracked fine-grained materials are possible to make with high strength and significantly increased thermal stress resistance, and also exhibit higher fracture energies than crack-free, dense, isotropic bodies. Thus, on a comparative basis with glass waste forms, improvement in the limits of dispersability would be expected with microstructure development programs to improve properties for the composition ranges of interest. However, as now understood, the desired microstructures for corrosion resistance are diametrically opposed to those needed for high strength. Hence, product engineering will require optimization based on needed data. Cermets should also be considered as a part of this group, with metal additions designed to provide a matrix phase which would increase the thermal conductivity of the composite. Further improvements in impact resistance and potentially reduced dispersability are to be expected with properly designed ceramic or cermet microstructures. For all crystalline composites considered in comparison with glasses, a higher initial thermal conductivity is attractive but is expected to degrade with time during interment due to radiation effects. For crystalline materials the problem with respect to helium blistering is expected to be worse than for a "homogeneous glass".

The processing system for multiphase polycrystalline composites will require some consolidation step for pelletization; the rotary pelletizer is proposed as a workable technique with a minimum of attendant problems in remote handling. Sintering operations involve similar requirements as for glass melting and are not envisioned to cause undue difficulties in remote handling. The addition of small contents of liquids to promote sintering or lower the sintering temperature has been demonstrated for many systems and may also be applicable to this technology area, although for the Sandia titanate process, the liquid present at the sintering temperature does not significantly enhance the rate or permit the use of lower temperatures. An adaptation of the sol-gel processes (developed for ThO_2 and UO_2) to provide for low sintering temperatures without a liquid phase is another possible alternative.

Hot pressing has been proposed as an alternate technique in order to achieve higher densities in the fabricated material at lower temperatures and shorter times than would be required for sintering. As an additional process step with increased mechanical handling required, further complications are envisioned for remote handling although they are not regarded as restrictive, i.e., confidence exists that such a system could be suitably engineered. It is envisioned that samples up to a foot in diameter could be fabricated at low pressure. However, the number of hot presses required and the pressing times govern the system through-put per unit volume; the process parameters will need further study before decisions can be made about overall process costs. (It was stated that contained volume dictates the capital cost to remote handling, the through-put being the second parameter affecting the product costs).

An alternate waste form envisioned is of small (approximately mm sized) polycrystalline beads which would be coated to provide high strength films, impermeable to fission product release and also corrosion resistant with respect to geologic ground waters. Pelletizing with a rotary pelletizer followed by a firing operation is envisioned. Coating by chemical-vapor-deposition (CVD) in a fluidized bed is

proposed for pyro-graphite and aluminum oxide. The CVD process has been developed for deposition of silicon carbide and pyro-graphite coatings for reactor fuels. Adaptation to waste form containment will only require engineering development for remote handling. This over-all process is presumed to be more complicated than those above simply because of the increased number of steps involved. An attractive prospect for this process is the potential development of a coating material like silicon nitride which is more resistant to swelling and blistering than are any of the other dense, close-packed materials, like aluminum oxide. There is also the prospect for the development of a material like alumina (isolated from the damage range) for the outer coating which may be more resistant to leaching than any of the matrix phases enclosed.

Ceramic pellets, glass pellets or coated ceramic beads may then be presumed to be packed into a canister within a metal matrix (lead or aluminum proposed) in order to decrease the temperature gradients within the casket during preliminary storage as well as after internment.

For all of these structures there is inadequate data on the leach resistance and on structural degradation under the simultaneous thermal and radiation conditions which will exist. The thermal conditions, however, are subject to modification by the engineering system. Metal matrix containment is expected to lower the peak center line temperatures achieved, but it is not now known whether higher temperatures would be more attractive because radiation damage annealing and helium release would be preferred.

GENERAL

Although various waste forms, glassy or ceramic or cermet are presumed capable of accommodating the distribution of waste products, there is a question about the capability (without further dilution) of a glass form to accommodate vastly increased gadolinium contents as may be required by the Nuclear Regulatory Commission provisions to reduce criticality in fuels reprocessing. Greater difficulty is expected for

incorporation of high gadolinium contents into glassy forms than in polycrystalline, poly-phase composites. If increased Gd content is required, an intensification of efforts on all waste composition systems are urgently needed in order to meet the deadlines for the development of demonstration containment systems.

The need for data generation on corrosion resistance, frangibility, thermal shock resistance, compatibility of the waste forms with the canister or metal matrix has been established by the other panels. The fabrication requirements for the production of test samples might well be designed to follow along the envisioned processes outlined above for the various prospective waste forms. Multiple composition ranges need to be identified for exploration, particularly in relationship to the variable geologic environments in which internment is envisioned. Much improved coordination with the community of geologists is needed to specify the variable ground water compositions and specific rock-soups with which stability is intended. Variable microstructures are then needed for the composite waste storage systems for testing. In general, it is assumed that these must be of high density, preferably of large grain size, potentially with controlled crack geometry (to control dispersability) and produced by processes with low temperature requirements. Thus exploration of sol-gel processing (as developed for thorium) adapted to the waste composition distribution would be useful, as well as the development of low temperature glasses to use for low temperature sintering operations or as glass containment systems.

EXPERIMENTAL METHODS, MODEL SYSTEMS, ACCELERATED TESTING

Group Members: R. Roy (Discussion Leader)
Y. Chen
L. Hobbs
L. Chick
R. M. Fulrath
W. A. Ross
P. B. Macedo
M. G. Britton
S. M. Wiederhorn

GROUP FINDINGS

The group noted that many of the following issues overlapped those of other sessions and hence should be read in conjunction with them.

SPECIFIC QUESTIONS

1. Given the complex time-temperature and radiation history, do we understand the behavior of glasses and ceramics to perform accelerated tests over short time periods to predict their behavior over hundreds or thousands of years? If so, what are the important parameters in tests for: leaching; thermal stability; radiation effects; and their combination? If not, what studies would be performed? Do we need to know mechanisms, activation energies, etc? Specifically?

The Table summarizes our opinions.

2. Can non-radioactive model systems be substituted for actual waste for various tests? If so, what compositions and what tests?

It was clear that for the large majority of experiments, non-radioactive models were perfectly satisfactory (obviously excepting self-heating effects).

3. What studies should be performed to provide information that can be used to predict glass and ceramic behavior over geologic time periods? Can the Oklo data be of help?

The direction of the information flow is more likely to go in the other direction. The geological data guide and put limits to the ceramic and glass information. Oklo data may serve as a calibrant to laboratory extrapolations. Waste and rock phase equilibrium data should be definitely determined for a small set of static environments, for 2 or 3 rock types, and 3 or 4 glass compositions.

4. Is basic research necessary? If so, in what areas?

It was clear that the most generally useful basic research would be the development of new instruments or tools to measure with maximum sensitivity the amount of H^+ , Cs^+ , Sr^{++} and other elements present. Without this, many different studies and advances on leaching or loss of major elements will be hampered.

TABLE 1

CAPACITY TO PREDICT OVER LONG RANGES

1. Radiation Effects α β γ Transmutation	Equipment and theory available to extrapolate from laboratory data.
2. Thermal Stability	Thermodynamic stability of any ceramic (and glass) assemblage under given pH, eH added solution or rock can be determined by relatively straightforward hydrothermal and dry equilibrium techniques known for 25 years. These are quite reliable from 350°C on up; below this it is more problematic, but excellent information on <u>directions</u> of equilibrium can be obtained. No extrapolation is needed since these are supposedly equilibrium data. While it will be extremely difficult to extrapolate with confidence any leach rates beyond the tens of years, with appropriate tools one can do careful work on mechanisms and products of leaching, and thence interpret more sensibly any rate data.
3. Leach Rates	Accelerated tests achieved by using substantially higher temperatures are very hazardous. It would, e.g., be useless to use data from 400°C to predict behavior at 60°C. Since reactions are therefore sure to be very slow, it is essential to have very precise tools which have both sensitivity and can sample 1-10 ⁸ thickness. H ⁺ and the alkalis are the keys to much of this behavior.

APPENDIX

AGENDA

ERDA Workshop Meeting on
"Ceramic and Glass Radioactive Waste Forms"

January 4-5, 1977

Germantown, MD.
Room E-401

Tuesday, January 4, 1977
Morning (9:00 a.m. - 12:30 p.m.)

"Waste Forms"

<u>Topic</u>	<u>Speaker</u>	<u>Approximate Time (min.)</u>
1. Introduction	D. Readey, C. Cooley	15
2. Overview of Waste Management	R. Ramsey/C. Cooley	30
3. Glass as a Waste Form	J. Mendel, W. Ross R. Turcotte	90
4. Ceramics and Glass-Ceramics as Waste Forms	G. McCarthy	30
5. The Oklo Phenomenon Implications Regarding Waste Forms	G. Cowan	30

Afternoon (1:45 p.m. - 5:15 p.m.)

"Material Properties"

<u>Topic</u>	<u>Speaker</u>	<u>Approximate Time (min.)</u>
6. Glass Structure Composition and Stability	D. Uhlmann	30
7. Metamict Mineral Alteration: Implications Regarding Waste Forms	R. Ewing	30
8. Radiation Damage in Ceramics	F. Clinard	20

<u>Topic</u>	<u>Speaker</u>	<u>Approximate Time (min.)</u>
9. Radiation Damage in Glass and Silicates	W. Primak	20
10. Leaching of Glass	L. Hench	30
11. Leaching & Alteration of Minerals	R. Vidale	30
12. Mechanical Properties of Glass & Ceramics	W. Wiederhorn	30

Wednesday, January 5, 1977
Morning (9:00 a.m. - 12:00 noon)

Group Discussion

<u>Area</u>	<u>Group Leader</u>
1. Leaching and Corrosion	L. Hench
2. Radiation Effects	T. Chikalla
3. Thermal Effects	A. Cooper

Group Reports 11:00 - 12:00 p.m.

Afternoon (1:00 p.m. - 4:00 p.m.)

4. Long Term Stability	V. Tennery
5. Waste Form, Composition, and Processing	R. Coble
6. Experimental Methods, Accelerated Testing, and Model Systems	R. Roy

Group Reports (3:00 p.m. - 4:00 p.m.)
Meeting Concludes at 4:00 p.m.

Group 1

Leaching and Corrosion

L. Hench

B. Adams
G. Cowan
K. Johnson
J. Kelley
C. Klingsburg
P. Macedo
J. Mendel
A. Rauscher
W. White
S. Wiederhorn
R. Vidale

Group 2

Radiation Effects

T. Chikalla

Y. Chen
F. Clinard
R. Ewing
L. Hobbs
P. Levy
W. Primak
R. Turcotte
C. Yust
V. Tennery
M. Kupfer

Group 3

Thermal Effects

A. Cooper

J. Barreth
L. Chick
R. Coble
R. Fulrath
D. Lam
G. McCarthy
W. Ross
R. Roy
J. Shelby
D. Uhlmann
M. Berard

Group 4

Long Term Stability

V. Tennery

G. Cowan
F. Clinard
R. Ewing
J. Shelby
D. Uhlmann
T. Chikalla
W. White
R. Vidale
W. Primak
L. Hench
A. Cooper

Group 5

Waste Form, Composition
and Processing

R. Coble

B. Adams
J. Barreth
D. Lam
G. McCarthy
M. Berard
J. Mendel
R. Turcotte
M. Kupfer
C. Yust
K. Johnson
C. Klingsburg

Group 6

Experimental Methods,
Accelerated Testing,
and Model Systems

R. Roy

Y. Chen
L. Hobbs
L. Chick
R. Fulrath
W. Ross
P. Macedo
J. Kelley
A. Rauscher
S. Wiederhorn
P. Levy

WORKSHOP PARTICIPANTS AND ATTENDEES

<u>NAME</u>	<u>ORGANIZATION</u>
P. B. Adams	Corning Glass
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J. R. Berreth	Idaho National Engineering Laboratory
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T. D. Chikalla	Pacific Northwest Laboratory
F. W. Clinard, Jr.	Los Alamos Scientific Laboratory
R. L. Coble	Massachusetts Institute of Technology
C. R. Cooley	ERDA/DWPR
A. R. Cooper	Case Western Reserve University
G. A. Cowan	Los Alamos Scientific Laboratory
W. K. Eister	ERDA/DWPR
R. P. Epple	ERDA/DPR
R. C. Ewing	University of New Mexico
R. M. Fulrath	University of California
S. M. Goldberg	Environmental Protection Agency
L. L. Hench	University of Florida
W. M. Hewitt	Nuclear Regulatory Commission
L. Hobbs	Case Western Reserve University
J. K. Johnstone	Sandia Laboratories, Albuquerque
J. A. Kelley	DuPont Savannah River Laboratory
C. Klingsburg	Atlantic Richfield Hanford Company
M. J. Kupfer	Atlantic Richfield Hanford Company
D. J. Lam	Argonne National Laboratory
P. W. Levy	Brookhaven National Laboratory
W. E. Lotz	ERDA/DWPR
G. J. McCarthy	Pennsylvania State University
P. Macedo	Catholic University
J. E. Mendel	Pacific Northwest Laboratory
R. Milstein	National Academy of Sciences
W. Primak	Argonne National Laboratory
R. W. Ramsey	ERDA/DWPR
D. W. Readey	ERDA/DPR
W. A. Ross	Pacific Northwest Laboratory
R. Roy	Pennsylvania State University
J. E. Shelby	Sandia Laboratories, Livermore
D. Y. Smith	Argonne National Laboratory
V. J. Tennery	Oak Ridge National Laboratory
R. P. Turcotte	Pacific Northwest Laboratory
D. R. Uhlmann	Massachusetts Institute of Technology
R. Vidale	Los Alamos Scientific Laboratory
R. D. Walton, Jr.	ERDA/DWPR
W. B. White	Pennsylvania State University
S. M. Wiederhorn	National Bureau of Standards
C. S. Yust	Oak Ridge National Laboratory