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**Quarterly Progress Report
Research and Development
Activities Waste Fixation
Program
January through March 1977**

by
J. L. McElroy

November 1977

Prepared for the
U.S. Department of Energy
under Contract EY-76-C-06-1830

Battelle

Pacific Northwest Laboratories

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QUARTERLY PROGRESS REPORT
RESEARCH AND DEVELOPMENT ACTIVITIES
WASTE FIXATION PROGRAM 111
JANUARY THROUGH MARCH 1977

by
J.L. McElroy

November 1977

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PREVIOUS REPORTS

This progress report is the eighteenth in a series that presents research and development activities in radioactive waste fixation. Previous progress reports were BNWL-1699, 1741, 1761, 1788, 1809, 1826, 1841, 1871, 1893, 1908, 1932, 1949, 1994, 2070, 2242, 2243, and 2264.

SUMMARY

Research and Development activities of the Waste Fixation Program for January through March 1977 are described in this report. The objective of this program is to develop processes to convert high-level radioactive liquid waste (HLLW) to solid forms that are demonstrated to be physically, chemically, and radiolytically stable and inert.

Several significant results were obtained during this reporting period. These are listed below and detailed in this report.

- An engineering-scale in-can melting (ICM) run was made that demonstrated a melting rate of 65 kg/hr in a 16-in. diameter can containing internal fins.
- The incorporation of chopped zircaloy hulls in ICM process glass canisters was demonstrated on a small scale by two methods.
- The large-scale direct liquid fed ceramic melter started up in early February. Preliminary tests demonstrated that the tilt-drain concept was functional.
- Devitrification phases of the low-zinc waste glass (76-68) remain at concentrations of less than 3 vol% after 2 months at 500 to 900°C.
- The first full-level radioactive glass specimens have been leached for over four months. The leach rates decrease in the order ^{137}Cs , $^{90}\text{Sr} > ^{239+240}\text{Pu} > ^{244+243}\text{Cm}$.
- While demonstrating feasibility of the concept, the quality of fluidized-bed coatings of multibarrier waste forms has been inconsistent; thus other methods, such as drum coaters, are being evaluated.

CONTENTS

PREVIOUS REPORTS	ii
SUMMARY	iii
INTRODUCTION	1
SECTION 1 - WASTE FIXATION PROCESS DEVELOPMENT	2
IN-CAN MELTING	2
SPRAY CALCINER DEVELOPMENT	3
ZIRCALOY CLADDING DISPOSAL USING IN-CAN MELTING	4
PROGRESS ON SAFETY ANALYSIS FOR SPRAY CALCINATION/ IN-CAN MELTING	4
CANISTER DEVELOPMENT PROGRAM	6
FLUIDIZED-BED CALCINATION	6
JOULE-HEATED CERAMIC MELTER	8
SECTION 2 - WASTE FORM CHARACTERIZATION	9
MELT DEVELOPMENT	9
COMBINATION WASTES	9
THERMAL EFFECTS ON STORED GLASS	11
ENGINEERING-SCALE GLASS CHARACTERIZATION	11
ENVIRONMENTAL REACTIONS OF WASTE GLASS	14
Acid-Base Durability	14
Long-Term Leach Rates	15
High Temperature and Pressure Tests	15
FULL-LEVEL RADIOACTIVE TESTS	16
FULL-LEVEL RADIOACTIVE GLASS CHARACTERIZATION	16
PHASE BEHAVIOR	17
WASTE VAPORIZATION STUDIES	20
MECHANICAL AND THERMAL SHOCK	23
Impact Testing	23
Mechanical Strength Measurements	25
Thermal Shock Properties	27
NEUTRON RADIOGRAPHY DEMONSTRATION	29
STANDARD TESTS	31
LEACHING OF IRRADIATED LWR FUEL PELLETS	31

CONTENTS (contd)

SECTION 3 - ALTERNATIVE WASTE FIXATION PROCESSES	34
ENGINEERING FEASIBILITY	34
CHEMICAL VAPOR DEPOSITED COATINGS	36
DISK PELLETIZER EVALUATION	37
Supercalcine Cores	38
Glass Frit Coated Cores	38
GLASS MARBLE DEVELOPMENT	38
METAL MATRIX	39
CHARACTERIZATION OF MULTIBARRIER WASTE FORMS	40
Vaporization	40
Impact Resistance	40
Leachability	43
RADIATION DAMAGE	45
SUPERCALCINE	45
Characterization of Supercalcine SPC-2	46
Phase Formation in SPC-2	46
Hot Pressed SPC-2	47
SPC-2 Plus Uranium	48
Cesium Aluminosilicates	49
REFERENCES	51

LIST OF FIGURES

1	In-Can Melter Capacity	3
2	Soxhlet Leach Rate Versus Storage Temperature 76-68 Glass	12
3	Closed Porosity Distribution	14
4	Leach Rate of 72-68 Glass in Distilled Water at 25°C Based on Uranium Behavior	15
5	Comparison Between Leach Rates of Sr, Cs, Pu and Cm	18
6	Weight Loss in Dry Air	21
7	Weight Loss After 12 hr in Dry Air	22
8	Impact Test Comparisons of ICM-11 Simulated Waste Glass 76-101 Frit with Previous Data, at Two Impact Energies	24
9	Comparison of Impact Test Results for Restricted- Stroke and Normal Impact Tests on Fused Silica and Soda-Lime-Silica Glass	25
10	Size Distribution (Equivalent Spherical Diameter) on -44 μ m Soda-Lime Silica Glass Particles Produced by Impact at 158 ft-lb	26
11	Schematic of ASTM Test Method C496-64T	26
12	Thermal Expansion Curves for Annealed Samples of 73-1 Frit, 76-101 Frit, and ICM-11 Simulated Waste Glass	28
13	Neutron Radiographs of 1 x 4-in. Cylinders of Borosilicate Waste Glass	30
14	Leach Rate of Zorita Fuel Pellet Fragments Normalized to Behavior of ^{137}Cs	33
15	Waste Loading in a Canister 10 ft long x 1 ft in diameter	35
16	Compaction of 0.50-in.-Diameter Matrix Samples Upon Impact	41
17	Particle-Size Distribution for Fractured Glass Portion of Pb-10Sn Matrix Samples	42
18	Surface Area Versus Impact for Uncoated Supercalcine Cores and Waste Glass and Soda-Lime Marbles	43
19	X-ray Diffractogram Tracings of Compatibility Run CS-94 and Supercalcine SPC-2 after Identical Firings of 1125°C for 2.5 hr in Air	47

LIST OF TABLES

1	Composition of Representative High-Level Radioactive Wastes After Conversion to Calcine	10
2	Composition of Cold Engineering-Scale ICM Runs	13
3	Acid-Base Durability of Waste Glasses	15
4	Glassmaker Off-Gas Data for 100-g Batch of PW-ZORITA(1:3)73-1 Glass	17
5	Glass Composition (wt%)	20
6	Weight Loss in 4 hr at 1100°C in Dry Air for Different Glasses	21
7	Thermal Expansion Parameters	28
8	Chemical Analysis of Instant Ocean Synthetic Sea Salt	32
9	Description of Supercalcine Leach Samples	44
10	Leach Results for SPC-2 Samples	44

QUARTERLY PROGRESS REPORT
RESEARCH AND DEVELOPMENT ACTIVITIES
WASTE FIXATION PROGRAM
JANUARY THROUGH MARCH 1977

INTRODUCTION

The objective of the High-Level Waste Fixation Program is to provide the technological bases which will enable the implementation of fully appropriate techniques for the conversion of high-level radioactive waste to stable, non-dispersible solid forms such as silicate glasses. The program is designed to be a means through which users of the technology and government can cooperate in an effective and optimum approach to this common problem. These objectives are being accomplished by a comprehensive program which includes: development and characterization of glass formulations; development of equipment and processes and design, construction and demonstration of full-scale process equipment.

The research and development activities in radioactive waste fixation for the reporting period of January through March 1977 are described in this report.

SECTION 1 - WASTE FIXATION PROCESS DEVELOPMENT

The purpose of this task is to develop processes and equipment for converting liquid high-level radioactive waste to a stable, relatively nondispersible form for storage and, ultimately, disposal. This objective is generally being accomplished by development of a two-step approach (calcination or concentration) followed by melting to form a silicate glass.

IN-CAN MELTING (H. T. Blair and W. J. Mikols)

The purpose of this study is to further develop and demonstrate on a full scale the vitrification of calcined high-level nuclear waste using the storage can as the melting crucible.

A melting rate of greater than 65 kg/hr was demonstrated in the single-zone, engineering-scale furnace using a 16-in.-diameter can containing a drop-in, radial, cooling fin assembly of 8 fins. Figure 1 shows the melting rate as a function of can diameter. That the slope of the curve in Figure 1 is constant suggests that the melting capacity of cans larger than 16-in. in diameter will be significantly higher. Thus, the ICM process becomes more practical for solidification of large-volume and low-heat-content defense wastes.

Fabrication of the first two cans to be used in the full-scale ICM began. One can will have a 12-in. diameter and the other a 16-in. diameter. Both cans will be suspended in the furnace from the lid of the retort. Following the processing of these two cans, the full-scale ICM will be modified to support the can at the bottom while it is in the furnace. Bottom support permits the use of thinner-walled cans and makes it possible to locate the entire can inside the furnace. A connecting section, which swings on a rotating seal, will also be included for demonstration at that time in the full-scale solidification system. This movable connector will permit the furnace to remain stationary, thus eliminating the need for flexible service leads to the furnace and a portable load cell system.

FIGURE 1. In-Can Melter Capacity

During the past quarter, the use of a protective furnace retort was tested in pilot-scale equipment. The retort served as a chamber for an inert cover gas during the ICM heating process. This arrangement significantly reduced the amount of steel canister spall that normally occurs at elevated process temperatures. The retort did appear to alter furnace temperature distributions at low temperatures. As higher temperatures were approached, radiative heat transfer dominated. Consequently, no significant change in furnace temperature gradients resulted because of the retort.

SPRAY CALCINER DEVELOPMENT (L. S. Romero)

The objective of this work is to provide a reliable system for conversion of HLLW-ILLW to calcine for vitrification.

Several runs were conducted to:

- evaluate a cyclone separator, thus simplifying the filtering system
- evaluate a feed system which does not require a feed rate control valve
- evaluate an external mix nozzle, which eliminates a pressurized feed line (elimination of feed pump).

The tests were positive and work is being continued.

ZIRCALOY CLADDING DISPOSAL USING IN-CAN MELTING (W. J. Mikols)

The purpose of this study is to investigate the process feasibility of incorporating chopped zircaloy hulls in canisters of HLW glass.

During the past quarter the ICM process equipment was modified so that chopped zircaloy hulls could be combined with HLW glass. Hulls were added by two methods: 1) combined with the ICM glass frit feed stream, and 2) dropped into a molten pool of glass in the ICM canister. Both schemes seem to be plausible for use with the small-scale ICM process tested. Very little product void formation was noticed as a result of hull addition. As a result of hull addition, a significant amount of microcracking occurred in the glass.

PROGRESS ON SAFETY ANALYSIS FOR SPRAY CALCINATION/IN-CAN MELTING (A. K. Postma and A. A. Garrett)

The objective of this work is to evaluate the safety aspects of a particular process for solidification of high-level radioactive wastes. The processes being studied involve calcination of HLLW using a radiant wall spray calciner, with subsequent formation of borosilicate glass within an ICM.

During this reporting period, work focused on developing an approach to be used in identifying and quantifying the most important accident and off-standard situations applicable to the process. A feasible approach to be used in this work includes:

- identification of a series of accident classes that can be used to catalog all possible incidents
- identification of a number of accidents or off-standard situations representative of each accident class

- evaluation of the consequences of the most important accidents in each class (including the magnitude of an airborne or liquid source term)
- comparison of the accidents, and on the basis of consequences and probability, identification of those that are most important.

Accident classes identified to date are:

Class 1. Trivial Accidents

Class 2. Incidents Involving Greater than Normal Source Terms Released Into Intact Cleanup Systems

A. Release Into Vessel Vent System

B. Release Into Cell Ventilation System

Class 3. Incidents Involving Failure of Cleanup Systems

A. Failure of Vessel Vent System

(1) Normal Source Term

(2) Above-Normal Source Term

B. Failure of Cell Ventilation System

(1) Normal Source Term

(2) Above-Normal Source Term

C. Coincident Failure of Vessel and Cell Vent Systems

Class 4. Incidents Involving Release of Effluents Into Operating Gallery

A. Gallery Vent System Undamaged

(1) Cell and Vessel Vent Systems Undamaged

(2) Cell and/or Vessel Vent Systems Damaged

B. Gallery Vent System Damaged

(1) Cell and Vessel Vent Systems Undamaged

(2) Cell and/or Vessel Vent Systems Damaged

At this time, work is under way to identify specific incidents in each accident class and then to determine source terms for each accident. A preliminary evaluation of all accidents will be made to identify the most important ones. A more detailed analysis is planned for those accidents inadequately analyzed to date.

CANISTER DEVELOPMENT PROGRAM (S. C. Slate)

The purpose of this work is to develop suitable canisters and related technology for containment of solidified HLW.

Canister development activities are divided into two areas: analysis and data acquisitions and engineering demonstration. Significant progress was made in all areas of the program this quarter; major efforts were in the areas of stress analysis and the closure system design.

The stress analysis work is concerned with determining the physical properties of various canister materials and computer modeling of the stresses in canisters under various conditions. The physical properties of 304L and Inconel 601 have been identified to an extent that enables formulation of design stress as a function of temperature. The computer modeling effort has been very intensive this quarter. 12-, 16-, 20-, and 24-in.-diameter canisters are being modeled during processing and handling. Areas being looked at include wall thickness, corner design, and the effects of outside forces.

Work on the canister closure system is proceeding ahead of schedule. Design of the canister top and lid for 12-, 16-, 20-, and 24-in.-diameter canisters is complete and fabrication of canisters for the full-scale spray calciner/ICM system has started. Purchase specifications for the remote welder were completed and bids have been solicited.

One of the most important new activities started this quarter is the design of equipment for the evaluation of full-sized canisters in simulated water storage conditions. It is planned to place 12-in.-diameter by 7-ft-long canisters in test pods that simulate various water conditions. The purpose of this is to obtain long-term corrosion performance information on actual sized canisters.

FLUIDIZED-BED CALCINATION (W. J. Bjorklund, J. C. Hartl and F. E. Haun)

Fluidized-bed calcination studies provide data for process and equipment development in the conversion of high-level waste to a solidified form. The calcine product can then be fed directly or indirectly to a melting system for vitrification.

Several runs were made during this period on the pilot-scale fluidized-bed calciner. Highlights include:

- A modified external mix fuel nozzle was successfully tested.
- A new combustion control system was installed and tested on the fluidized-bed calciner.
- A quench scrubber off-gas system was evaluated while coupled to the fluidized-bed calciner.
- Continuous inert bed operation⁽¹⁾ continues to provide excellent operating characteristics.

Several projects are being completed:

- A new and independent off-gas system should be in operation shortly. The system includes a series of venturi scrubbers for gas stream cleanup.
- An airlift feed system has been designed and components fabricated. Installation is expected to be completed in the near future.
- An improved cyclone is being tested in the off-gas system. This cyclone cleans the off gas before final filtration with sintered metal filters.

Future developments will include:

- Completion of design and construction of a higher capacity fluidized bed. This calciner will also operate in the continuous inert bed mode and will be coupled with a continuous ceramic melter.
- Off-gas characterization by computer calculations of equilibrium and nonequilibrium chemical compositions in the fluidized-bed calciner.
- On-line off-gas analysis by gas chromatography.
- Use of formic acid feed denitration.

JOULE-HEATED CERAMIC MELTER (C. C. Chapman, J. L. Buelte and R. D. Dierks)

The objective of this work is to develop a reliable ceramic melter that can be used for converting radioactive waste to glass.

The engineering-scale ceramic melter was shut down after 12 months of operation since restart in January 1976. The refractories and electrodes have now been exposed to molten glass for 23 months. The portion of the sidewall that collapsed did not result in loss of containment. Exposure of the backup refractory to the molten glass occurred for approximately nine months. This suggests that water cooling of the sidewalls is an excellent barrier to the potential escape of molten glass. Destructive examination of the melter is planned but has not been completed.

The large-scale direct liquid-fed melter was started up in early February and a new startup technique was demonstrated. The melting cavity in this melter is 34 in. wide, 48 in. long and 28 in. deep with a nominal glass depth of 19 in. The melting cavity is powered by two independently controlled electrode banks. One set rests on the floor and the top set is 3 in. below the molten glass surface. The top and bottom electrodes are 8 and 4 in. high respectively and span the entire width of the melting cavity. The two sets are separated by 4 in. of refractory.

The drain is composed of a hole in the large riser block and a 12-in.-long trough. Drainage of glass is started and stopped by tilting the entire melter $\pm 2^\circ$. Preliminary tests have successfully demonstrated its functionality.

A plant-scale ceramic melter is currently being designed that will be coupled to a large-scale fluidized-bed calciner. The unit is being designed to process 50 to 70 kg of glass/hr.

SECTION 2 - WASTE FORM CHARACTERIZATION

The purpose of waste form characterization is to measure the properties of candidate solidified products (solidified waste and canister) as functions of composition, processing parameters, and storage conditions. The measurements are used: 1) to assure operability of the manufacturing processes, and 2) to provide data for safety analyses of high-level waste management. The ultimate goal is to characterize the physical and chemical properties of the waste forms so thoroughly that when they are placed in retrievable storage, and later in ultimate disposal, full confidence can exist that their behavior is known and that any changes or any interactions with their environment which may occur are wholly predictable.

MELT DEVELOPMENT (W. A. Ross and E. T. Sherman)

The objective of this work is to develop melt compositions suitable for incorporating HLW in durable glasses at low process temperatures.

Melt development was started on three new waste compositions, PW-7c, PW-7d and PW-9. The new waste compositions are given in Table 1. Waste compositions used previously in melt development are also shown in the table for comparison. The main distinguishing characteristics of PW-7c and PW-7d are, 1) increased gadolinium content, and 2) the presence of Zircaloy fines. PW-9 is a variation of a "clean" waste somewhat similar to PW-4b.

COMBINATION WASTES (E. T. Sherman)

The purpose of this work is to evaluate the potential for combining high-level, intermediate-level and transuranic incinerator ash into a single waste glass form.

Glasses containing a simulated AGNS high-level waste, PW-7c-1, and TRU incinerator ash have been made. The combination wastes glasses contain 33 wt% PW-7c-1 and 1 to 3 wt% ash. The melts are judged on homogeneity, viscosity and leachability. The best melt to date is melt 77-115 (34 wt%

TABLE 1. Composition of Representative High-Level Radioactive Wastes After Conversion to Calcine

		Kilograms Oxide/MTU										
		PW-4b	PW-4c	PW-6	PW-7	PW-7a	PW-7b	PW-7c	PW-7d	PW-8	PW-8a	PW-9
Inerts	Na ₂ O	-	1.126	23.459	0.117	6.872	6.872	7.972	6.737	5.857	14.057	5.857
	Fe ₂ O ₃	1.511	1.511	15.112	3.022	3.022	17.711	3.046	0.179	39.895	27.225	1.508
	Cr ₂ O ₃	0.345	0.345	1.295	0.345	0.345	0.345	0.045	0.050	1.151	1.151	0.345
	NiO	0.141	0.141	0.566	0.141	0.141	0.141	0.020	0.023	0.566	0.566	0.141
	P ₂ O ₅	0.672	0.672	0.672	2.686	6.339	6.339	5.901	5.02	1.340	1.340	0.671
	Al ₂ O ₃	-	83.937 ^(a)	-	-	-	-	-	-	-	-	-
	MnO ₂	-	-	-	-	-	-	0.266	0.225	-	-	-
	Gd ₂ O ₃	-	-	-	10.360	10.360	10.360	25.767	37.963	-	-	-
	Zr-II Fines	-	-	-	-	-	-	0.338 ^(b)	0.333	-	-	-
	SUBTOTAL	2.669	87.732	41.104	16.671	27.079	41.768	43.688	50.535	48.779	44.339	12.90
Fission Products (same for all wastes)	Rb ₂ O	-	-	-	0.354 ^(c)	-	-	0.275	0.391	-	-	0.424
	SrO	-	-	-	1.059	-	-	0.724	1.099	-	-	1.214
	Y ₂ O ₃	-	-	-	0.598	-	-	0.438	0.572	-	-	0.683
	ZrO ₂	-	-	-	4.944	-	-	3.777	5.321	-	-	5.589
	MoO ₃	-	-	-	5.176	-	-	3.933	5.581	-	-	5.984
	Tc ₂ O ₇	-	-	-	1.291	-	-	1.036	1.397	-	-	1.337
	RuO ₂	-	-	-	2.972	-	-	2.157	3.055	-	-	3.720
	Rh ₂ O ₃	-	-	-	0.480	-	-	0.405	0.486	-	-	0.528
	PdO	-	-	-	1.483	-	-	1.237	1.653	-	-	1.989
	Ag ₂ O	-	-	-	0.088	-	-	0.056	0.067	-	-	0.079
	CdO	-	-	-	0.097	-	-	0.070	0.102	-	-	0.141
	TeO ₂	-	-	-	0.725	-	-	0.547	0.751	-	-	0.845
	Cs ₂ O	-	-	-	2.880	-	-	1.989	2.937	-	-	3.356
	BaO	-	-	-	1.567	-	-	1.380	1.433	-	-	1.913
	La ₂ O ₃	-	-	-	1.480	-	-	1.127	1.574	-	-	1.786
	CeO ₂	-	-	-	3.323	-	-	2.291	3.323	-	-	4.034
	Pr ₆ O ₁₁	-	-	-	1.482	-	-	1.092	1.546	-	-	1.802
	Nd ₂ O ₃	-	-	-	4.522	-	-	3.613	5.037	-	-	5.469
	Pm ₂ O ₃	-	-	-	0.123	-	-	0.026	0.083	-	-	0.149
	Sm ₂ O ₃	-	-	-	0.924	-	-	0.824	1.034	-	-	1.120
	Eu ₂ O ₃	-	-	-	0.200	-	-	0.141	0.221	-	-	0.240
	Gd ₂ O ₃	-	-	-	0.137	-	-	0.087	0.149	-	-	0.165
	SUBTOTAL	35.905	35.905	35.905	35.905	35.905	35.905	27.225	37.812	35.905	35.905	42.565
Actinides	U ₃ O ₈	1.169	1.169	5.738	11.689	11.689	11.689	12.897	12.8935	5.526	11.689	5.623
	NpO ₂	0.865	0.865	0.865	0.865	0.865	0.865	0.167	0.612	0.865	0.865	0.702
	PuO ₂	0.010	0.010	0.051	0.103	0.103	0.103	0.122	0.1243	0.051	0.174	0.083
	Am ₂ O ₃	0.181	0.181	0.181	0.181	0.181	0.181	0.144	0.174	0.181	0.181	0.252
	Cm ₂ O ₃	0.040	0.040	0.040	0.040	0.040	0.040	0.007	0.044	0.040	0.040	0.101
	SUBTOTAL	2.265	2.265	6.875	12.878	12.878	12.878	13.337	13.39	6.663	12.949	6.768
TOTAL		40.8	125.9	83.0	65.5	75.9	90.6	84.250	99.1	91.35	93.2	57.85

(a) Seed particles used as starting bed in fluidized-bed calciner.

(b) Will be solid Zr metal in waste stream.

(c) Fission products noted by dash are the same as PW-7.

SiO₂, 9 wt% B₂O₃, 8 wt% Na₂O, 2 wt% CaO, 2 wt% K₂O, 6 wt% TiO₂, 3 wt% CuO, 3 wt% ash, and 33 wt% PW-7c-1). Based on these preliminary tests combining high-level waste and Tru incinerator ash in a single waste glass appears feasible.

THERMAL EFFECTS ON STORED GLASS (J. H. Westsik, Jr.)

The purpose of this work is to determine changes in properties of HLW glass as functions of storage time and temperature.

Elevated temperature storage of 76-68 glass through two months is completed. These samples are currently undergoing characterization.

Soxhlet leach rates as a function of storage temperature for 76-68 glass are plotted in Figure 2. The curve for each storage period does not show the well-defined peak observed for the 72-68 glass.⁽²⁾ The "as-formed" sample (1050°C for 2 hr) of 76-68 glass had a 5.80 wt% loss (7.4×10^{-5} g/cm²-day) in the Soxhlet test. Within experimental error, the leach rates for the as-formed and the stored glass samples are the same. From this information it may be concluded on a preliminary basis that storage of 76-68 glass at elevated temperatures does not affect the leach rates of the glass.

ENGINEERING-SCALE GLASS CHARACTERIZATION (Y. B. Katayama and J. H. Westsik, Jr.)

The purpose of this project is to characterize waste glasses produced on an engineering-scale in the Waste Fixation Program.

In-can melts 16 and 18 are currently being characterized. Samples from each canister were taken longitudinally every 6 in. In ICM-16 the samples were taken 1/2 in. from the wall and equidistant between two fins. At the 24-in. level, samples were also taken radially toward the center of the melt. In ICM-18 the samples were taken along the centerline. Radial samples were taken at the 12-in. level. X-ray fluorescence analysis and closed porosity measurements have been completed for the samples.

FIGURE 2. Soxhlet Leach Rate
Versus Storage Temperature
76-68 Glass

Both optical microscope examination and SEM analysis show marked differences in the glass from the two canisters. These differences can be explained by comparing the composition of the glass in the two ICM runs, as shown in Table 2. The increased rare earth content in ICM-16 resulted in a greater amount and size of rare earth rich phases in ICM-16 compared to ICM-18. The ruthenium in ICM-18 was found to be mostly combined with tellurium in small metallic spheres. A few particles of nearly pure ruthenium were also found. The tellurium was found to be combined with nickel or ruthenium most of the time. A combination of the three elements was not found.

ICM-18 has many small iron rich particles dispersed throughout the canister. Some of these particles contain various amounts of chromium. ICM-16 had

TABLE 2. Composition of Cold Engineering-Scale ICM Runs

	ICM-16		ICM-18	
	Oxide Wt%	Metal Wt%	Oxide Wt%	Metal Wt%
Na ₂ O	3.79	2.81	5.92	4.39
Cr ₂ O ₃	0.17	0.12	0.45	0.31
P ₂ O ₅	3.11	1.36	0.53	0.23
SrO	1.92	1.62	1.82	1.54
ZrO ₂	2.44	1.81	1.94	1.44
Ag ₂ O	0.04	0.04	--	--
CdO	0.05	0.04	0.04	0.04
TeO ₂	0.36	0.29	0.28	0.22
BaO	2.17	1.94	2.01	1.80
Co ₃ O ₄	0.15	0.11	0.12	0.09
NiO	0.51	0.40	0.58	0.46
Fe ₂ O ₃	2.37	1.66	10.68	7.47
K ₂ O	4.43	3.68	3.94	3.27
MoO ₃	3.13	2.09	2.49	1.66
Cs ₂ O	--	--	1.13	1.07
RuO ₂	--	--	0.12	0.09
Rare Earths (as Ce)	15.75	12.82	8.36	6.81
B ₂ O ₃	10.60	3.29	10.60	3.29
CaO	1.40	1.00	1.40	1.00
MgO	1.40	0.84	1.40	0.84
ZnO	20.27	16.28	20.27	16.28

a thin layer of product containing nonspherical bubbles at the bottom of the canister. Figure 3 shows the distribution of closed porosity in the canisters.

There was a zone 1-1/2 in. deep at the bottom of ICM-16 that contained spalled layers of oxidized stainless steel. The slivers of oxide were up to 1/2 in. long by 1/32 in. wide. Above this zone the stainless steel oxide was found as small circular looking particles. These circular particles, containing iron, chromium and nickel, were also found dispersed throughout ICM-18.

FIGURE 3. Closed Porosity Distribution

ENVIRONMENTAL REACTIONS OF WASTE GLASS (J. H. Westsik, Jr.)

The objective of this task is to determine the leaching behavior of waste glass if it becomes exposed to the environment.

Acid-Base Durability

Natural ground waters have a pH ranging from 4 to 9. To test waste glass durability in acidic and basic solutions, glass samples are leached 19 hr in an ammonium hydroxide buffered solution of pH 9 followed by an additional 19-hr leach in an acetate buffer of pH 3.9.⁽²⁾ Both tests are done at room temperature.

Table 3 shows the results for glasses 72-68 and 76-68. The latter shows a significantly improved acid-base durability.

TABLE 3. Acid-Base Durability of Waste Glasses

		% Weight Loss	Test Time, hr	$\text{g/cm}^2\text{-day}$
72-68	PW-4b-6(2.8:1)73-1			
pH	9.0	3.59	19	1.74×10^{-4}
pH	3.9	93.43	19	4.53×10^{-3}
76-68	PW-8a-3(2:1)76-101			
pH	9.0	0.16	19	7.76×10^{-6}
pH	3.9	0.17	19	8.25×10^{-6}

Long-Term Leach Rates

Glass leach rates based on uranium behavior for 72-68 glass have been measured and are plotted in Figure 4. The leach rates are a factor of ten lower than those obtained by following cesium and strontium behavior for the same glass. Devitrification increased the uranium leach rates a factor of four rather than the factor of ten for cesium and strontium leach rates.

High Temperature and Pressure Tests

An autoclave system has been assembled to leach test waste glasses at the temperatures and pressures typical of geologic formation. The leachant is a salt solution similar to that which might come in contact with the glass in a salt formation. Preliminary data show a bulk leach rate of $7.2 \times 10^{-4} \text{ g/cm}^2\text{-day}$ for 72-68 glass and $3.1 \times 10^{-3} \text{ g/cm}^2\text{-day}$ for a soda-lime-silica glass (NBS #710).

FIGURE 4. Leach Rate of 72-68 Glass in Distilled Water at 25°C Based on Uranium Behavior

FULL-LEVEL RADIOACTIVE TESTS (Y. B. Katayama)

Fully radioactive waste glass specimens are being prepared on a laboratory scale. The off-gas is being analyzed during melting of the radioactive glass. Characteristics of the fully radioactive glass specimens will be compared with nonradioactive glasses of similar chemical composition as a function of storage conditions.

The material collected from the off-gas stream during two glassmaking runs and one calcining run was analyzed. A major portion of the volatilized material was collected on the water-cooled platinum chill plate located at the top of the melting chamber. An effusion plate separated the melt crucible and chill plate.

Table 4 shows the concentration in the caustic and water scrubber solutions and the nitric acid solution of the chill plate condensate. The percent volatilized was calculated on the basis of calcine composition at date of separation. This would give lower volatilization numbers for the rapidly decaying isotopes. Volatility descended in the order Se > Sb > Tc > Te > Cs > Ru.

FULL-LEVEL RADIOACTIVE GLASS CHARACTERIZATION (D. J. Bradley and C. E. Bigelow)

Leach rates resulting from the first seven months of leaching HLW glass wafers have been calculated for strontium, cesium, plutonium, and curium. The remainder of the fission products are currently being analyzed.

The leach solutions have been analyzed to date for the three principal fission products ^{90}Sr , ^{137}Cs , and ^{134}Cs and major actinide α emitters, $^{239+240}\text{Pu}$, $^{244+243}\text{Cm}$ and ^{242}Cm . Leach rates have been calculated from this data and Figure 5 shows a comparison between the leach rates of strontium, cesium, plutonium, and curium for the section of glass coming from the top of the melted glass cylinder. The remainder of the major fission products such as cesium and europium are currently being analyzed following cesium removal. From analyzing the leach rates from different sections of the glass column, it appears that the glass is quite homogeneous.

**TABLE 4. Glassmaker Off-Gas Data for 100-g
Batch of PW-ZORITA(1:3)73-1 Glass**

Element Volatilized	Concentration in Calcine ^(a)	Chill Plate	Caustic Scrub	Water Scrub	Percent Volatilized
• Run CW-6 ^(b) 72-68 Glass					
Te	$3.12 \times 10^5 \mu\text{g}$	100 μg	<400 μg	10 μg	0.16
Se	$2.23 \times 10 \mu\text{g}$	232 μg	156 μg	16 μg	18.1
Sb	$5.42 \times 10 \mu\text{g}$	17 μg	<40 μg	4.4 μg	11.3
Tc	$5.83 \times 10^{-4} \text{ Ci}$	$1.25 \times 10^{-5} \text{ Ci}$	$1.66 \times 10^{-6} \text{ Ci}$	$2.70 \times 10^{-6} \text{ Ci}$	2.89
¹³⁷ Cs	17.9 Ci	$2.72 \times 10^{-2} \text{ Ci}$	$3.16 \times 10^{-2} \text{ Ci}$	$4.33 \times 10^{-3} \text{ Ci}$	0.35
¹³⁴ Cs	15.47 Ci	$1.74 \times 10^{-2} \text{ Ci}$	$2.03 \times 10^{-2} \text{ Ci}$	$3.06 \times 10^{-3} \text{ Ci}$	0.26
¹⁰⁶ Ru	6.73 Ci	$2.12 \times 10^{-3} \text{ Ci}$	$1.41 \times 10^{-3} \text{ Ci}$	--	0.05
• Run CW-7 ^(c) 72-68 Glass					
Te	$3.12 \times 10^5 \mu\text{g}$	1350 μg	<400 μg	6 μg	0.56
Se	$2.23 \times 10^3 \mu\text{g}$	495 μg	<40 μg	32 μg	25.4
Sb	$5.42 \times 10^2 \mu\text{g}$	4.5 μg	<40 μg	1.6 μg	8.5
Tc	$5.83 \times 10^{-4} \text{ Ci}$	$4.05 \times 10^{-6} \text{ Ci}$	$1.19 \times 10^{-6} \text{ Ci}$	$1.98 \times 10^{-6} \text{ Ci}$	1.24
¹³⁷ Cs	17.9 Ci	$6.11 \times 10^{-2} \text{ Ci}$	$2.61 \times 10^{-2} \text{ Ci}$	$3.26 \times 10^{-3} \text{ Ci}$	0.50
¹³⁴ Cs	15.47 Ci	$3.72 \times 10^{-2} \text{ Ci}$	$1.60 \times 10^{-2} \text{ Ci}$	$2.17 \times 10^{-3} \text{ Ci}$	0.24
¹⁰⁶ Ru	6.73 Ci	--	--	--	--
• Run CW-8 ^(d) Calcining					
Te	$1.25 \times 10^6 \mu\text{g}$	60 μg	<400 μg	2.8 μg	0.004
Se	$8.92 \times 10^3 \mu\text{g}$	45 μg	108 μg	3.84 μg	1.76
Sb	$2.17 \times 10^3 \mu\text{g}$	7.5 μg	80 μg	3.2 μg	4.18
Tc	$2.33 \times 10^{-3} \text{ Ci}$	$4.39 \times 10^{-8} \text{ Ci}$	$2.88 \times 10^{-8} \text{ Ci}$	$3.60 \times 10^{-8} \text{ Ci}$	0.005
¹³⁷ Cs	71.61 Ci	$1.07 \times 10^{-4} \text{ Ci}$	$8.73 \times 10^{-4} \text{ Ci}$	$3.19 \times 10^{-4} \text{ Ci}$	0.002
¹³⁴ Cs	61.89 Ci	$7.66 \times 10^{-5} \text{ Ci}$	$5.92 \times 10^{-4} \text{ Ci}$	$2.17 \times 10^{-4} \text{ Ci}$	0.001
¹⁰⁶ Ru	26.92 Ci	$7.78 \times 10^{-4} \text{ Ci}$	$9.94 \times 10^{-4} \text{ Ci}$	--	0.006

(a) Concentration in calcine is not corrected for decay and represents concentration at separation.

(b) Run CW-6, 70 min heatup time, 6 hr at 1050°C.

(c) Run CW-7, 195 min heatup time, 3 hr at 1050°C.

(d) Run CW-8, calcination run, 1 hr at 500°C.

PHASE BEHAVIOR (J. W. Wald and R. P. Turcotte)

This task is directed toward general understanding of the glassmaking and devitrification processes. The effort is aimed primarily toward examination of phase separation by microscopy, microprobe analysis and x-ray diffraction methods.

FIGURE 5. Comparison Between Leach Rates of Sr, Cs, Pu and Cm

During this quarter, microstructural and electron microprobe examination of the full-level reference waste glass (72-68) was completed at Battelle Columbus Laboratories (BCL) and the complete data to date have been reviewed. Qualitative x-ray diffraction examination on long-term anneal samples of glass 76-68 (NFS) has also been performed.

Microprobe analysis on crystallites in full-level waste glass sample CW-6 indicated that the primary phase present is Zn_2SiO_4 . Appreciable rare earth concentrations were indicated (i.e., neodymium, lanthanum) in some of the Zn_2SiO_4 analyses. Based on experience with simulated glasses, this is expected since a rare earth apatite phase has been seen to grow from Zn_2SiO_4 crystals.

The secondary devitrification product SrMoO_4 seen in simulated glasses does not appear in the full-level system; however, this is likely because the molybdenum concentration is very low. A secondary microstructural form has been identified in this glass; microprobe analysis suggests that this is an apatite type compound $[\text{Ca}_2(\text{Re})_8(\text{SiO}_4)_6]$ containing uranium, neodymium, calcium, silicon, and possibly cerium. The morphology appears different than the apatite phase observed in the simulated system (dendritic as opposed to feathery); however, with the exception of uranium, the elemental composition is similar. It is felt at this point that examination work at BCL on these first full-level samples is complete. The differences observed between the radioactive glass and simulated nonradioactive glasses are explainable from compositional differences. With the exception of the uranium-containing dendrite phase in CW-3, all other phases present were expected.

Isochronal anneals have been performed on glass (76-68) for 1-day, 1-week, and 2-month time periods between the temperature range of 500 to 900°C. The major crystalline phases seen to this point are RuO_2 , a cubic-fluorite related phase $(\text{U,Ce})\text{O}_2$, and a spinel phase $(\text{Fe,Cr,Ni})_3\text{O}_4$. After 1 day at temperature, the RuO_2 phase concentration remains relatively constant with increasing temperature. The spinel phase reaches a maximum at 700°C and seems to decrease with higher temperatures. The fluorite phase appears at 800°C, increases about twofold at 850°C, and is not present at 900°C and 1 day.

The behavior at 1 week's time resembles 1 day at temperature for RuO_2 and spinel; however, the fluorite phase appears at 600°C and increases in concentration with temperature. After 2 months at temperature, a fourth phase is observed at lower temperatures (600 to 750°C) for which structure type assignments have not yet been made.

For the most part, the crystalline phases present have been seen to exist at relatively low concentration levels (<3% per phase). No major new phases have appeared and for this time-temperature matrix, the glass continues to have favorable thermal stability. During the next quarter, phase concentrations will be quantitatively established.

WASTE VAPORIZATION STUDIES (W. J. Gray)

The purpose of this study is to investigate the vaporization behavior of wastes containing fission products during processing, shipment, and storage. Accident conditions involving high temperatures and breach of the container during shipment or storage are of particular interest.

Table 5 lists compositions of glasses being studied to test a hypothesis that TiO_2 additions reduce cesium volatility. Gross weight-loss data at 1000°C were reported for these melts earlier,⁽²⁾ and it was shown that gross weight loss increased with increasing TiO_2 content. Figure 6 shows gross weight-loss data for two of these melts in the range 1000 to 1200°C . A greater difference occurs between the two at 1100°C than at either higher or lower temperatures, but even at 1100°C , the difference is small.

Table 6 lists weight losses of individual elements from three of the glasses listed in Table 5 and from 72-68 glass for comparison. Data for the latter and descriptions of experimental procedures were reported previously.⁽³⁾ Data listed in Table 6 for 72-68 glass are the average of duplicate runs whereas data for each of the other glasses are based on only one run. Thus, somewhat larger uncertainties apply to the latter. Nevertheless, it is clear from the data presented here that TiO_2 additions to the 76-238 glass formulation have only a small effect on the volatility of cesium or any of the other elements; furthermore, the effect is in the wrong direction.

TABLE 5. Glass Composition (wt%)

Melt No.	SiO_2	B_2O_3	TiO_2	Al_2O_3	Na_2O	K_2O	CaO	CuO	PW-7a Calcine
76-238	41.5	9.5	-	1	8	2	2	3	33
76-239	38.5	9.5	3	1	8	2	2	3	33
76-240	32.5	9.5	9	1	8	2	2	3	33
76-241	29.5	9.5	12	1	8	2	2	3	33
76-242	35.5	9.5	6	1	8	2	2	3	33

FIGURE 6. Weight Loss in Dry Air

TABLE 6. Weight Loss in 4 hr at 1100°C
in Dry Air for Different Glasses

Element	72-68		76-238 (0% TiO ₂)		76-242 (6% TiO ₂)		76-241 (12% TiO ₂)	
	mg/cm ² (a)	Percent (b)	mg/cm ² (a)	Percent (b)	mg/cm ² (a)	Percent (b)	mg/cm ² (a)	Percent (b)
B	0.55	1.57	0.76	2.58	0.65	2.20	0.92	3.12
Na	0.32	1.05	0.48	0.57	0.50	0.59	0.57	0.68
K	1.34	3.90	0.82	4.92	0.96	5.76	1.25	7.50
Rb	0.18	8.53	0.11	6.66	0.11	6.66	0.14	8.48
Mo	0.27	0.94	0.17	0.80	0.14	0.66	0.21	0.99
Ru	0.072	0.48	0.42	3.75	0.24	2.14	0.36	3.21
Te	0.76	19.79	0.40	13.89	0.46	15.97	1.17	40.63
Cs	4.58	25.42	1.88	13.84	2.18	16.05	3.07	22.60

(a) Absolute weight loss per unit area for 2.0 g sample with 2.0 cm² surface area.

(b) Percentage weight loss based on amount of element originally present.

Table 6 also shows that, with the exception of ruthenium, the volatility of fission products from 76-238 glass is less than from 72-68 glass. Figure 7 shows that the total weight loss from 76-238 is slightly less than from 72-68 and that the difference increases with decreasing temperature.

FIGURE 7. Weight Loss After 12 hr in Dry Air

MECHANICAL AND THERMAL SHOCK (L. R. Bunnell)

The purpose of this work is to examine factors relevant to the thermal and mechanical shock resistance of waste-containing glasses and to suggest methods for possible improvement in these properties.

Impact Testing

Impact testing of glasses continued by the same methods outlined previously.⁽²⁾ Diamond coring and cutoff equipment was installed so that uranium-containing glasses can be handled. This quarter, impact testing was done on 76-101 frit and on samples from ICM-11. Figure 8 summarizes all of the data to date, including these new glasses, at two impact energies. The most impact-resistant glass evaluated to date is 76-101 frit; fused silica is still the worst; and ICM-11 is not greatly different from its parent frit (73-1). The crystalline phases present in ICM-11 glass lower its impact resistance (probably by decreasing its strength). The reason for glass-to-glass differences is not yet clear; apparently it is not simply related to the silica content since 76-101 frit contains more SiO_2 than 73-1 frit but performs better, while pure silica is the worst glass in impact.

The impact generated by the testing machine is complex, and is in reality several impacts. Since the specimen is only 0.44 in. in diameter, contained in a 1-in.-diameter cavity, the first impact breaks it and spreads it on the bottom of the cavity, where the final impact occurs. To gain an appreciation of these two events, some plungers were made such that their stroke was limited, i.e., they could only travel 0.010, 0.025, 0.050, or 0.1 inches. None of these stroke lengths brings the plunger into contact with the debris from the first impact, so it can be examined separately. As expected, little difference occurred among the results produced by these four strokes. Figure 9 compares restricted-stroke impact data with normal data tests performed at the same hammer speed (16 ft/sec) on soda-lime-silica glass. The energy is not determinate with a restricted-stroke plunger. The interesting feature is that a fairly large amount of fine material ($<37 \mu\text{m}$) is produced by a restricted impact. The energy imparted to the glass at the moment of impact is apparently released in a very violent manner.

FIGURE 8. Impact Test Comparisons of ICM-11 Simulated Waste Glass 76-101 Frit with Previous Data, at Two Impact Energies

FIGURE 9. Comparison of Impact Test Results for Restricted-Stroke and Normal Impact Tests on Fused Silica and Soda-Lime-Silica Glass

Regarding respiration hazards, glass particles less than $\sim 10 \mu\text{m}$ are a major concern. The screen analysis used for the main characterization has its limitations in the -325 mesh ($-44 \mu\text{m}$) range, where static charge effects, etc., can produce erroneous results. A sedimentation type particle-size analyzer (Micromeritics 5000) operated by the Hanford Engineering Development Laboratory (HEDL) was used to size the $-44 \mu\text{m}$ fraction (9.7 wt%) of some soda-lime-silica glass impacted at 158 ft-lb; Figure 10 shows the results. The $-44 \mu\text{m}$ cutoff diameter from the screens was fairly accurate; also essentially no particles exist less than $\sim 1.5 \mu\text{m}$ in diameter. The $-10 \mu\text{m}$ fraction amounts to $(20\% \times 9.7\%) = 1.9 \text{ wt\%}$ of the total.

Mechanical Strength Measurements

The core-drilled specimens made for impact testing provide an opportunity to examine the strength of waste glass. ASTM test method C496-64T provides an attractive means for evaluating the strength of these cylinders and is shown schematically in Figure 11. The cylinder is automatically self-aligning, and the

FIGURE 10. Size Distribution (Equivalent Spherical Diameter) on -44 μm Soda-Lime-Silica Glass Particles Produced by Impact at 158 ft-lb

FIGURE 11. Schematic of ASTM Test Method C496-64T

specimen breaks in tension along its vertical midplane. The figure also shows pads at the top and bottom of the specimen; these are necessary to prevent severe point loads that would otherwise occur where the glass touches the steel

platens. A number of materials, such as copper, lead, brass, plastics, plywood, several papers and hardwoods, were examined for use as pads. Most soft polymers and some soft metals, such as lead, were extruded by the high forces at contact points, but properly oriented balsa wood, 1/16 in. thick, proved to be an effective pad material. Other investigators⁽⁴⁾ have determined that 0.005-in.-thick copper is an effective pad material, but the balsa worked better in our case, as determined by higher ultimate stresses and lower standard deviations.

Specimens of soda-lime-silica glass tested this way showed an average strength of 10,870 psi and a standard deviation of 1400 psi. Samples cored from ICM-11 showed an average strength of 6303 psi and a standard deviation of 1370 psi. The many crystalline particles in ICM-11 glass contribute to its lower strength.

Thermal Shock Properties

Thermal expansion runs were completed on 73-1 and 76-101 frits and on a piece of glass near the central axis of in-can melt run ICM-11. The former two had been annealed according to a standard schedule (500°C for 2 hr, furnace cooled), and the latter was "annealed" by being near the center of a large thermal mass. The expansion curves for the three are shown in Figure 12. The samples are well annealed as shown by the absence of dips in the curves near the glass transition temperatures. Poorly annealed specimens show a dip close to the glass transition temperature as they tend toward their equilibrium density. Table 7 shows some pertinent data extracted from the curves. It is seen that 76-101 has a lower expansion coefficient and a higher softening point, as would be expected from its higher SiO_2 content, and that the addition of calcine to 7-31 frit has not altered its first two properties to a large extent but has increased the expansion coefficient.

The possibility of severe thermal stress cracking in glass waste forms has caused some concern. The temperature cycle of the vitrification processes, together with the fairly high thermal expansion of the waste glass composition, effectively preclude the production of a true monolith. A few cracks will occur in the best case, as shown below. The use of fins in the ICM process

FIGURE 12. Thermal Expansion Curves for Annealed Samples of 73-1 Frit, 76-101 Frit, and ICM-11 Simulated Waste Glass

TABLE 7. Thermal Expansion Parameters

	73-1	76-101	ICM-11
Glass Transition Temperature, °C	510	563	520
Dilatometric Softening Point, °C	560	615	565
Average Expansion Coefficient to 400°C	8.13×10^{-6}	7.20×10^{-6}	9.33×10^{-6}

helps greatly in the melting process, but the imperfect match of thermal expansion coefficients produces a series of cracks around each fin. Disregarding fins for the present, the expression

$$\Delta T = \frac{2\sigma(1-\mu)}{E\alpha}$$

where T = temperature difference, °C

σ = breaking stress, taken as 6300 psi^(a)

μ = Poisson's ratio, taken as 0.25

E = Young's modulus, taken as 10×10^6 psi

α = thermal expansion coefficient, $9.33 \times 10^{-6}/^\circ\text{C}$, measured on ICM-11

(a) See page 27

gives the maximum ΔT that can be sustained by a slab of any thickness without fracture, assuming the slab is not allowed to bend. Introduction of the values above yields a temperature of about 100°C. A few cracks are thus inevitable, but the surface area generated by this cracking is small when compared to the expansion mismatch cracks at fins and canister wall. We are attempting to quantify the surface area increase from all thermal cracking. In actual heat-generating waste, the thermal gradient and the resulting cracking should be less severe. It is desirable to define a more complete axial thermal profile of a finned canister than has been done to date. This will be explored in the near future.

NEUTRON RADIOGRAPHY DEMONSTRATION (J. W. Voss and L. R. Bunnell)

A canister full of high-level waste glass is a challenging subject for nondestructive examination. The canister may contain internal features such as cracks, voids, precipitates and fins, but the high radiation fields make inspection very difficult. X-radiography, for instance, is certainly prevented. Neutron radiography, however, is not affected by the high gamma radiation fields and was evaluated using two facilities, one at the University of Arizona and the other operated by General Electric Company at Vallecitos, CA.

The examination of the feasibility of neutron radiography as a nondestructive testing method on borosilicate waste glass canisters done at the University of Arizona utilized the TRIGA reactor. The neutron radiography facility is a beam tube, which when placed on top of the core graphite reflector, transmits a low intensity thermal neutron beam. Initial experiments with small glass shapes about 1/4-in.-thick showed that metallic inclusions purposely put in the glass specimens could be detected easily. Differences in boron content (3 and 10 wt%) could also be detected. Cylinders of glass 1-in. in diameter by 4 in. long were also prepared with metallic inclusions and the two boron contents. Some of the cylinders were water quenched to produce fractures in the glass. A neutron radiograph of five of these cylinders is shown in Figure 13. Voids are clearly visible, but smaller cracks are not. Neither differences in boron content nor the presence of metallic inclusions can be detected in these thicker specimens.

FIGURE 13. Neutron Radiographs of 1 x 4-in.
Cylinders of Borosilicate Waste Glass

In order to obtain a further state-of-the-art neutron radiography result, the bottom section of ICM-18, containing drop-in fins, was sent to General Electric. The boron present in the waste glass prevented any effective neutron radiography, even with image enhancement techniques. Only the fins were visible. A few small images (1/16 in.) were noted which appeared to be pores or other features of low absorption, but G.E. personnel interpreted these as artifacts. For purposes of comparison, conventional x-radiography of ICM-18 was performed at the Hanford Engineering Development Laboratory; these radiographs showed the fins and areas of relatively high and low x-ray absorption which were presumably inhomogeneities in the glass. Neutron radiography thus appears not to be a feasible nondestructive testing method for full-sized canisters of borosilicate waste glass.

STANDARD TESTS (J. M. Rusin)

The purpose of this study is to develop tests to compare various waste form products. Efforts are being directed toward developing a combined impact-leachability test.

To combine a leaching and impact test, a suitable material must be found to contain the fine particulate produced upon impact. Past efforts have been directed to a polycarbonate filler membrane, Nuclepore. Problems from faulty heat seals were eliminated by use of Silastic Medical Adhesive Silicone Type A for the seals. Upon further testing it was observed that the basic solution created by glass dissolution attacked the Nuclepore membrane. Use of Nuclepore membrane has discontinued and efforts have been directed toward ultrafine metal screens.

LEACHING OF IRRADIATED LWR FUEL PELLETS (Y. B. Katayama)

Irradiated fuel fragments are being leach-tested and the results will be correlated with similar information about common solidified HLW forms.

Fuel fragments from the Zorita Reactor with a burnup of 54,450 MWd/MTU are being leach-tested in a brine solution. The brine solution was made from

dissolving Instant Ocean^(a) salt in deionized water. Table 8 presents the manufacturer's reported ionic composition.

After 28 days the leach rate, normalized to ^{137}Cs behavior, is 1.86×10^{-5} g/cm²-day in a Paige type leach apparatus. The leach rate is graphically shown in Figure 14; the early portions of the leach rate curves for the same fuel in Hanford ground water, building distilled water and deionized water are also shown. The leach rate in brine approximates the leaching trend in deionized water.

TABLE 8. Chemical Analysis of Instant Ocean Synthetic Sea Salt

A solution of Instant Ocean Synthetic Sea Salt adjusted to a specific gravity of 1.025 at 15°C has the following ionic composition:

<u>Chemical</u>	<u>ppm</u>	<u>Chemical</u>	<u>ppm</u>	<u>Chemical</u>	<u>ppm</u>
Cl	18,400	Sr	6.0	Rb	0.10
Na	10,220	SiO ₃	3.0	I	0.07
SO ₄	2,518	PO ₄	1.3	EDTA	0.06
Mg	1,238	Mn	1.2	Al	0.04
K	390	F	1.0	Zn	0.02
Ca	370	MoO ₄	0.6	V	0.02
HCO ₃	142	S ₂ O ₃	0.3	Co	0.01
Br	60	Li	0.2	Fe	0.01
H ₃ BO ₃	25			Cu	0.003

(a) Instant Ocean is a copyrighted name for a synthetic sea salt manufactured by Aquarium Systems, Inc.

FIGURE 14. Leach Rate of Zorita Fuel Pellet Fragments Normalized to Behavior of ^{137}Cs

SECTION 3 - ALTERNATIVE WASTE FIXATION PROCESSES

The goal of this task is to develop alternative waste fixation processes and evaluate their waste form products to assure that viable backup processes to the mainline processes will be available if needed. The alternative processes and products are to be compared for cost and safety to the current reference process and product, silicate glass castings in large metal canisters. The alternative processes are being developed on the laboratory scale. In the concept currently emphasized the waste is formed into small granules or pellets which are coated with nonradioactive inert materials to provide containment and leach resistance. The coated waste shapes are then incorporated into a metal matrix which provides impact resistance and increased thermal conductivity.

ENGINEERING FEASIBILITY (R. O. Lokken)

The engineering feasibility study is designed to develop and correlate process procedures necessary to achieve the objective of the multibarrier concept (i.e., enhanced inertness). Evaluation of equipment needs, complexity, and adaptability to remote operation follows closely with the first purpose. Comparison of the multibarrier products with glass and calcine products will be based on economic and cost/benefit studies.

An engineering feasibility study was started for three multibarrier composite waste forms. The three basic waste forms being considered are:

- PyC/Al₂O₃ CVD-coated supercalcine in a gravity-sintered stainless steel matrix,
- glass-frit-coated supercalcine in a gravity-sintered bronze matrix,
- waste glass marbles in a vacuum cast lead or aluminum alloy matrix.

Preliminary process flow rates were calculated for the three processes. However, because of the number and uncertainties of the process parameters and the complexity of the processes, the calculations can only be used as a basis of comparison between the different waste forms. As more confident and/or accurate values of process parameters are identified, subsequent calculations

need to be made to update mass flow and heat flow values. A computer program is currently being developed to perform these calculations and to determine material requirements, storage equipment sizes, and material costs. The program will handle the three pellet types with a choice of six matrix metals.

Additional calculations were made that relate supercalcine core diameter and coating thickness to waste loading in coated pellets. Figure 15 shows the weight of waste in a canister 10 ft (305 cm) long by 1 ft (30.5 cm) in diameter. Curves are plotted for frit-coated and PyC/Al₂O₃ CVD-coated supercalcine pellets as a function of uncoated pellet diameter and coating thickness. The waste loading in uncoated supercalcine is 75 wt%. The waste loading in a canister of glass marbles containing 35 wt% waste is also included in the figure.

FIGURE 15. Waste Loading in a Canister 10 ft long x 1 ft in diameter

CHEMICAL VAPOR DEPOSITED COATINGS (M. F. Browning)^(a)

The purpose of this study is to demonstrate that simulated radioactive calcined waste particles in a size range of 1 to 10 mm can be provided with coatings designed to protect them under the environmental condition expected during long-term storage. The approach has been to apply appropriate coatings such as Al_2O_3 and/or PyC to supercalcinced particles using chemical vapor deposition processes with fluidized-bed and/or mechanically-agitated particle techniques.

As discussed last quarter, a problem was encountered in obtaining crack-free duplex coatings on the available supercalcinced waste even though impervious coatings of PyC and Al_2O_3 individually had been satisfactorily applied to waste particles. This cracking problem was thought to result from a thermal expansion mismatch between the Al_2O_3 outer coating and the PyC/substrate.

The initial approach explored this quarter to overcome the cracking problem has been to: 1) minimize infiltration of the substrate porosity by the coating and thus retain its inherent crushability, 2) provide a low-density PyC coating with a lower elastic modulus, 3) deposit a friable porous Al_2O_3 layer between the PyC and outer density Al_2O_3 coating, and 4) apply a dense Al_2O_3 coating of sufficient thickness (strength) to resist cracking and force the other components of the system to yield. As a result of this effort a procedure has been developed for applying an Al_2O_3 /PyC coating to a batch of supercalcinced simulated waste particles that lost only 0.08 wt% at 750°C in air after 115 hr. In this batch (32556-79-99) a 32- μ m PyC coating on a 2-mm SPC-2 particle was overcoated with a 7- μ m porous Al_2O_3 layer and finally with a 47- μ m dense Al_2O_3 outer coating. The PyC coating was deposited from C_2H_2 at 1100°C, and the porous and dense Al_2O_3 coating from the hydrolysis of $AlCl_3$ at 550 and 1050°C, respectively. All coatings were applied by a fluidized-bed technique.

Later in the quarter the duplex coating procedure was further refined so that a protective duplex coating was satisfactorily applied without including a porous Al_2O_3 buffer layer. A batch (32556-84-101) prepared in this manner lost only 0.012 wt% at 750°C in air after 11.5 hr. This batch was prepared with SPC-2 particles nominally 2-mm in diameter and had a 78- μ m Al_2O_3 /39- μ m PyC duplex coating.

(a) Battelle Columbus Laboratories

As an alternative to the fluidized-bed technique, it was decided to first evaluate a simple rotating drum system, which consists of a rotating 22-mm quartz tube. The particles to be coated are confined to a central section of this tube by perforated graphite disks. During the application of Al_2O_3 , the reactants, AlCl_3 , CO_2 , and H_2 , were introduced through the graphite disk at one end of the tumbling particle bed and the reaction products were removed at the opposite end. AlCl_3 was introduced in one end of the rotating tube. The AlCl_3 was generated by passing HCl through aluminum strips at $<600^\circ\text{C}$. This design permitted the required rotating seals to operate at essentially ambient temperature while the coating section was heated by electric furnace. A graphite spacer bar for the disks at each end of the particle coating section was positioned against the wall of the reactor and acted as a lifter bar to the tumbling particles. A brief study of barrel design indicated that the design chosen was the best of those examined for minimizing areas of low particle density; this allows excessive by-passing of the reactants.

This unit was operated using the 3- to 5-mm SPC-2 supercalcine simulated waste particles, which were received late in the quarter, after heat treating them at 1125°C for 6 hr in air. Since CO_2 and H_2 were used ($\text{CO}_2 + \text{H}_2 \rightarrow \text{H}_2\text{O} + \text{CO}$) as the hydrolysis agent instead of the water vapor used in the fluidized-bed work, it was necessary to deposit the Al_2O_3 at $>1100^\circ\text{C}$. Below this temperature the CO_2/H_2 reaction proceeds slowly. Using the CO_2/H_2 system is advisable in coating systems (other than fluidized-bed) because it tends to minimize gas-phase nucleation and promote surface reactions. The unit was operated without encountering significant difficulties and $\sim 12\text{-}\mu$ dense-appearing Al_2O_3 coatings were obtained on the substrates. The quality of these coatings has yet to be ascertained.

DISK PELLETIZER EVALUATION (J. M. Lukacs, A. A. Garrett and C. B. Ruhter)

The purpose of this task is to evaluate the disk pelletizer as a means of: 1) forming spherical pellets from calcined waste material, and 2) coating sintered pellets in preparation for incorporation in a metal matrix.

Supercalcine Cores

Kilogram quantities of SPC-2 spherical cores (0.5-8 mm) have been produced using the disk pelletizer with established operating parameters. Approximately 2 kg of sintered cores were sent to Mr. M. L. Browning at BCL. Core density and durability were improved by adding bentonite as a binder and by increasing pellet water content; neither change adversely affected the supercalcine phases.

The pelletizing behavior of supercalcine is a function of calcine powder properties and equipment operating parameters. Changes in powder moisture content, homogeneity and grain size distribution can drastically upset pelletizer steady-state operation unless compensating process changes are made. Close control of powder properties will be necessary for remote operation.

Glass Frit Coated Cores

A glass frit coating can be applied to sintered cores with the disk pelletizer. Sintering these coated cores produced large fissures in the coating which penetrated to the core. Microscopic examination, thermal expansion data, and defects simulated in hand-prepared specimens indicate that the fissures resulted from extremely rapid volume shrinkage of the frit coating under the sintering conditions used. The sintering properties of frits used for coating and the supercalcine are being characterized. The goal is to decrease frit coating shrinkage and reduce the shrinkage difference between the core and coating, thereby eliminating cracking.

GLASS MARBLE DEVELOPMENT (J. M. Rusin)

The purpose of this study is to develop methods to produce waste glass marbles in remote facilities and to evaluate glass-metal matrix reactions. Waste glass marbles have been encapsulated in aluminum and lead alloys. Evaluation has been completed only for a Pb-10Sn alloy; the results show no evidence of reaction between glass and alloy.

Over 3 kg of simulated waste glass marbles, approximately 3/8-in. in diameter, have been produced by vibratory casting. Remelted ICM-11 glass was used, which is similar to the 72-68 composition. A small percentage of the marbles cracked because of chrome-spinel inclusions. However, since these

inclusions originate from canister corrosion, such cracking should not be a concern for conventionally melted glass. Negotiations are under way with Corning Glass Works to demonstrate continuous production of waste glass marbles by direct vibratory casting.

Simulated waste glass marbles have been encapsulated in Pb, Pb-10Sn, and Al-12Si by vacuum casting. The samples are being heat treated at temperatures up to 500°C and micrographs of heat-treated Pb-10Sn matrix samples have been completed. The samples were held at 200, 300, 400, and 500°C for 10 days. No reactions were observed except for some precipitation of selenium from the Pb-10Sn alloy during cooling of the 500°C sample.

METAL MATRIX (K. R. Sump)

The purpose of this study is to develop a metal matrix for increasing the thermal conductivity and impact strength of containers of HLW.

Properties of the various metal matrix candidates were compiled. Matrices considered for the glass marbles are aluminum and its alloys and lead and its alloys; matrices considered for the glass-coated supercalcine particles are cast aluminum and its alloys and gravity-sintered copper and its alloys. Stainless steels are the candidates for the Al_2O_3 - and PyC-coated supercalcine particles. The best all around matrix appears to be the cast aluminum alloys since they have good thermal conductivity, strength, corrosion resistance, and oxidation resistance. However, they have a moderately low melting point, a less desirable property. The aluminum alloys are very economical, second only to pure aluminum on a cost per volume basis.

Over 50 samples for characterization studies were vacuum cast in graphite molds during this quarter. Sample diameters were 9/16-, 1-1/4-, and 2-in.; matrices included pure aluminum, Al-12Si, pure lead, Pb-5Sn, and Pb-10Sn. Three and six-mm glass spheres were dispersed in all of these matrices. Waste glass marbles, 3/8 in. in diameter, were dispersed in the Al-12Si, Pb-5Sn and Pb-10Sn matrices. Pure metals without a ceramic phase were also cast for property studies. A sample of 6-mm glass spheres in a metal matrix of Al-12Si was

made where the amount of ceramic phase was 50% that of normal samples. All matrices appeared fully dense with the exception of pure aluminum and the 3- and 6-mm glass spheres.

Large, 2-in.-diameter samples of gravity-sintered copper and stainless steels without a ceramic phase were fabricated for thermal conductivity studies.

Besides the matrices currently being fabricated, the following will soon be used: 1) Pb-6Sb because of its lower cost when compared to Pb-Sn alloys, 2) Al-3.8 Mg because of its good resistance to sea water, and 3) aluminum bronze because of its resistance to sea water and its improved high temperature oxidation properties compared to other copper alloys.

CHARACTERIZATION OF MULTIBARRIER WASTE FORMS (J. M. Rusin)

The purpose of this study is to determine the physical, mechanical, and chemical properties of multibarrier waste forms for product optimization. Results are reported for impact resistance of matrix samples and supercalcine leachability.

Vaporization

Detailed vaporization studies have been started by W. J. Gray to include weight-loss data and collection of vapors on a cold finger for chemical analysis. Preliminary data on supercalcine powder was possibly influenced by the degree of sintering. Future work will therefore be done on pressed and sintered pellets so that the surface areas are the same in all cases.

Impact Resistance

A 410 stainless steel, gravity-sintered matrix containing 40% supercalcine loading instead of the normal 60% was impacted at 158.4 ft-lb to determine if reduction in loading can increase impact resistance. Visually, no significant improvements were observed with reduced loading. In both cases, the majority of the cores were pulverized. Although the loading was reduced to 40%, the effective increase in metal matrix was only from 20 to 30% since the matrix contains 50% porosity.

To demonstrate the resistance to compaction of 100% metal matrix, samples of gravity-sintered 410 stainless steel, Al-12Si, and Pb were impacted at various forces. The samples did not crack or break apart, but were compressed as a function of impact force as illustrated in Figure 16. As can be seen, the stainless steel matrix with 50% porosity offers excellent impact resistance when not diluted by the waste cores.

Screen analysis has been completed for the impacted Pb-10Sn matrix samples.⁽⁵⁾ The glass loading in the matrix was ~60 vol%. The weight percent of unfractured marbles for 10-mm waste glass, 6-mm and 3-mm chemical glass was 13.17%, 31.01%, and 76.35%, respectively. That the majority of the fractured glass had a particle size greater than 500 μm is illustrated in Figure 17. For the worst case, the weight percent less than 37 μ does not exceed 0.15%.

FIGURE 16. Compaction of 0.50-in.-Diameter Matrix Samples Upon Impact

FIGURE 17. Particle-Size Distribution for Fractured Glass Portion of Pb-10Sn Matrix Samples

Simulated waste glass marbles, soda-lime-glass marbles, and uncoated supercalcine cores were impacted in the apparatus developed by L. R. Bunnett.⁽⁵⁾ Results from sieve analysis had considerable scatter as the samples are highly pulverized upon impact and are agglomerated by the impact ram. An alternative to particle-size distribution is surface area created by impact. Surface area as determined by BET is plotted in Figure 18 for the impacted samples. Although the total surface area of supercalcine is much greater than that of waste glass or soda-lime marbles, the actual increase in surface area is less. The surface area for supercalcine, waste glass and soda-lime glass increases upon impact at 158.4 ft-lb by a factor of 4, 556, and 521, respectively.

FIGURE 18. Surface Area Versus Impact for Uncoated Supercalcine Cores and Waste Glass and Soda-Lime Marbles

Leachability

Supercalcine cores and pellets were leach tested for 72 hr by the Soxhlet and pH4 and pH9 static tests. Four differently prepared samples were tested as described in Table 9. Leach results are reported in Table 10 as total weight loss and in units of weight loss/cm²/day. The latter results are listed both for the typical initial surface area and for the final leached surface area. Further SEM analysis is being conducted on the samples and the leach solutions will be analyzed for specific ions.

TABLE 9. Description of Supercalcine Leach Samples

Samples	Preparation Technique	Typical BET Surface Area Before Test
C-1 to C-3	Disc pelletized 0.44-in.-diameter cores fired at 1150°C	1400 cm ² /gm
C-4 to C-6	Disc pelletized 0.35-in.-diameter cores, 5% Montmorillonite added; fired at 1150°C	350 cm ² /gm
SPC-2	Pressed at 20,000 psi; sintered at 1125°C for 6 hr, -42+60 mesh	530 cm ² /gm
SPC-2P	Prefired at 800°C for 1-1/2 hr, pressed at 20,000 psi; sintered at 1125°C for 6 hr, -42+60 mesh	380 cm ² /gm

TABLE 10. Leach Results for SPC-2 Samples

Sample	Leach Test (a)	Leached BET Surface Area	% wt Loss	Gm/cm ² /day (b)	Gm/cm ² /day (c)
C-1	Soxhlet	3600 cm ² /gm	0.64	5.93 x 10 ⁻⁷	1.52 x 10 ⁻⁶
C-2	pH9	2900	0.30	3.45 x 10 ⁻⁷	7.14 x 10 ⁻⁷
C-3	pH4	1600	0.31	6.46 x 10 ⁻⁷	7.38 x 10 ⁻⁷
C-4	Soxhlet	150	0.06	1.33 x 10 ⁻⁶	5.88 x 10 ⁻⁷
C-5	pH9	80	0.01	4.17 x 10 ⁻⁷	9.80 x 10 ⁻⁸
C-6	pH4	120	0.09	2.50 x 10 ⁻⁶	8.82 x 10 ⁻⁷
SPC-2-24	Soxhlet	3000	1.90	2.11 x 10 ⁻⁶	1.47 x 10 ⁻⁵
SPC-2-25	pH4	720	0.39	1.81 x 10 ⁻⁶	3.02 x 10 ⁻⁶
SPC-2-26	pH9	670	0.06	2.99 x 10 ⁻⁷	4.65 x 10 ⁻⁷
SPC-2P-1	Soxhlet	1800	0.93	1.72 x 10 ⁻⁶	8.16 x 10 ⁻⁶
SPC-2P-2	pH4	1200	0.49	1.36 x 10 ⁻⁶	4.30 x 10 ⁻⁶
SPC-2P-3	pH9	600	0.12	6.67 x 10 ⁻⁷	1.05 x 10 ⁻⁶

(a) All for 72 hr.

(b) Based upon leached surface area.

(c) Based upon typical initial surface area.

RADIATION DAMAGE (J. M. Rusin)

The purpose of this study is to determine the effects of radiation damage on the stability and physical properties of multibarrier waste forms. Doping of supercalcine with 3 wt% Cm²⁴⁴ has been completed. Procedures have begun to study possible transmutation effects by HFIR neutron irradiation.

Pellets of supercalcine doped with 3 wt% Cm²⁴⁴ have been pressed and sintered. Results from XRD indicate three new diffraction peaks that have not been identified. Stored energy and density measurements are being performed along with optical microscopy.

The steady-state temperature distribution of 0.29-in.-diameter samples for HFIR neutron irradiation was calculated with HEATING 4,⁽⁶⁾ a heat conduction code. Thermal power values were determined from the computer code ORIGIN.⁽⁷⁾ The calculated internal temperatures of simulated waste glass, pollucite, supercalcine, and SrMoO₄ did not exceed 200°C with external cooling by water at 16°C. Thorium silicate will not be irradiated since its calculated internal temperature exceeds 200°C.

Activities for the irradiated samples have been estimated from ORIGIN and range from 0.3 to 300 R/hr at 1 m. These levels of activity will require hot cell facilities. Changes in crystal phase and lattice parameter, as determined by XRD, are important observations in studying transmutation effects. Shielded XRD is not presently available; thus, the above measurements may not be made until a much later date.

SUPERCALCINE (G. J. McCarthy, The Pennsylvania State University)

The nature of the Penn State participation in the Alternative Waste Forms Program and the supercalcine concept has been described in previous reports. Current objectives of the Supercalcine Task include, 1) refinement of existing formulations for PW-4b and PW-7 wastes, 2) development of formulations for the high-sodium waste PW-7a, 3) determination of crystalline phase behavior of cesium, ruthenium, tellurium, palladium, and rhodium and the actinides in supercalcine, and 4) consideration of the effects of radiation and transmutation on supercalcine stability.

This contribution will focus on two subtasks, further characterization of the PNL engineering-scale "clean" supercalcine SPC-2 and preparation and characterization of cesium aluminosilicates.

Characterization of Supercalcine SPC-2 (G. J. McCarthy, D. E. Pfoertsch and M. Tason)

Crystalline phase formation, consolidation, thermal stability and soxhlet leachability were described in the last two Quarterly Progress Reports. Studies on verification of the phase formation model, hot pressing and uranium additions were completed this quarter.

Phase Formation in SPC-2

This formulation crystallizes on firing between 1000 and 1200°C into nine separate crystalline phases. The phases were identified by a combination of x-ray diffraction, scanning electron microscopy/electron microprobe and magnetic $[SP_{ss}]$ or thermal stability $[RuO_2]$ behavior. One of the surest methods to confirm these identifications, while at the same time testing phase compatibility under appropriate conditions, is to characterize the phase formation in increasingly more complete combinations of the exact proportions of SPC-2 components. It was decided to perform these tests as background for another demonstration scheduled for the summer of this year. The first combination of components were those involving the rare earths (RE,Ce). These were assigned the formation of $Ca_2RE_8[SiO_4]_6O_2 [A_{ss}] REPO_4 [M_{ss}]$ plus $(Zr,Ce...)O_2 [T_{ss}]$ plus $(Ce,Zr...)O_2 [F_{ss}]$. Firings at 1050, 1100 and 1200°C for 2 and 24 hr clearly showed the assigned crystalline phase in the x-ray diffractograms of the assemblage and confirmed the effective compatibility of its constituent phases. In similar fashion, the components assigned to the $(Cs,Rb,Na)AlSi_2O_6 [P]$, $(Ca,Sr,Ba)MoO_4 [S_{ss}]$ and $(Fe,Cr)_2O_3 [(Fe_2O_3)_{ss}]$ were added to the batch and the phases were identified in the diffractograms. Thus, all the SPC-2 phases observable by x-ray diffraction (SP_{ss} and RuO_2 were not) have been modeled and confirmed. Figure 19 shows a comparison of the final simulation run (CS-95) with SPC-2 crystallized under identical conditions. Each of the assigned phases is observed in both tracings. Again, it is notable that the spray calcine batch of SPC-2 yields a more crystalline produce than the laboratory-scale boil-down SPC-2 batch. This is due to the greater homogeneity derived from the flash decomposition of the solutions in the spray calciner.

FIGURE 19. X-ray Diffractogram Tracings of Compatibility Run CS-94 and Supercalcine SPC-2 after Identical Firings of 1125°C for 2.5 hr in Air. Reflections in CS-95 have been deconvoluted for clarity. The A_{SS} reflections are hatched and the M_{SS} reflections are cross-hatched. Note the sharper and more intense reflections in SPC-2, indicating greater crystallinity.

Hot Pressed SPC-2

Several hot pressing preparations are scheduled for each supercalcine formulation for two reasons: first, to obtain dense supercalcine specimens to measure properties (leachability, thermal conductivity, etc.), and second, to have some estimate of potential product improvements in case hot pressing will be considered further for HLW solidification.

SPC-2 was prefired at 900°C for 2 hr and then hot pressed at about 1000, 1100 and 1200°C and 3000 psi. Time at T_{max} was about 10 min. The 1000°C disc

was lighter in color than the others (brown versus black). The 1200°C disc had large pores in its interior, which suggested that gas was present during processing. Measured densities ($\pm 0.04 \text{ g/cm}^3$) were 3.67(1000), 4.12(1100) and 3.81(1200°C). The lower density of the 1200°C specimen can be attributed to the large pores.

X-ray characterization of the products showed poor crystallization at 1000, moderate to good at 1100 and very good at 1200°C. The near surface areas of the 1100 and especially the 1200°C pellets, which were also nearest to the graphite punch and die, showed far less F_{SS} and more A_{SS} than the interior regions. The Ce^{4+} in F_{SS} is reduced to Ce^{3+} ; this then reacts with available silica and is incorporated in A_{SS} . The pore rich region of the 1200°C specimen may be a result of the formation of CO from the reaction of oxygen released by the $CeO_2 \rightarrow Ce_2O_3$ reduction with the graphite tooling.

Weight losses in the 72 hr soxhlet leachability test were 3.53, 0.72 and 0.88% respectively for the 1000, 1100 and 1200°C preparations. The 1100°C run showed a small improvement over the 0.88% loss in the cold pressed and fired SPC-2.

SPC-2 Plus Uranium

The PW-7 series of wastes have comparatively high uranium concentrations. If the correct amount of uranium had been included in SPC-2 (0.1195M, which includes extra uranium as a substitute for neptunium and plutonium), uranium as U_3O_8 would constitute about 16 wt% of the product. To make SPC-2 representative in its uranium concentration, the appropriate amount of a uranyl nitrate solution was added to dried SPC-2 powder to form a slurry that was next calcined and fired (as pellets) at 1000 to 1200°C for 2.4 hr. The relative intensity of the crystalline phases in the diffractograms of the 1125°C firings of SPC-2 with and without uranium are:

SPC-2		SPC-2 + U	
S-F _{SS} (5.37Å)	M-S _{SS}	VS-F _{SS} (5.39Å)	M-S _{SS}
S-A _{SS}	MW-M _{SS}	M-T _{SS}	W-(Fe ₂ O ₃) _{SS}
M-T _{SS}	W-(Fe ₂ O ₃) _{SS}	M-M _{SS}	Amorphous Halo.
M-P		M-P	

The uranium oxide was incorporated in F_{SS} as expected. The striking difference is the absence of the A_{SS} phase. One explanation could be that a $U-F_{SS}$ has a stronger RE^{3+} affinity than does a silicate A_{SS} . The amorphous phase could be the released SiO_2 combined with other oxides in a noncrystalline form. However, M_{SS} is present, so apparently RE^{3+} prefers to form M_{SS} with the available $[PO_4]$ rather than F_{SS} . One must be careful, however, in generalizing the uranium crystal chemical role from SPC-2, because this formulation was prepared at PNL (for economic reasons) with three times the PW-7 ratio of cerium and with a corresponding reduction in RE^{3+} . The cerium would almost certainly prefer substitution as Ce^{4+} in F_{SS} to form $(U,Ce,Zr)O_{2+x}$. The RE^{3+} species could still be more stable in an A_{SS} . This was later confirmed with a series of compatibility studies in which it was found that a $(U,Ce)O_{2+x}-F_{SS}$ phase was compatible with A_{SS} at supercalcine crystallization temperatures. Extra steps are being taken to assure that the cerium concentration of the upcoming PNL supercalcine demonstration is representative of PW-7 waste.

The 72-hr soxhlet leachability weight losses of SPC-2 + U specimen crystallized at 1125°C for 2.4 hr averaged 0.75%, compared to 0.88% for pure SPC-2 crystallized under the same conditions. This reduction could be due to nothing more than the dilution of the leachable species with UO_2 . The leachate was clear and showed no sign of U^{4+} oxidation and subsequent leaching.

Cesium Aluminosilicates (S. A. Gallagher and G. J. McCarthy)

The aluminosilicates appear to be the best hosts for cesium in supercalcine, HLW glass ceramics and certain other nuclear applications. Major progress has been made on structure and phase characterization of two of these phases, $CsAlSiO_4$ and $CsAlSi_2O_6$ (pollucite).

Until now, no unambiguous unit cell or structure type had been assigned to $CsAlSiO_4$. The recently reported structure of $RbAlSiO_4$ ⁽⁸⁾ provided a potential model for the structure of $CsAlSiO_4$. All x-ray powder data could be indexed on an analogous unit cell:

A computer routine was used to calculate the powder pattern of CsAlSiO_4 using the RbAlSiO_4 atomic positions. The R-factor for the calculated and observed integrated intensities was 0.10. This is good agreement considering the approximate nature of the atomic positions.

The structure is composed of an ordered Al-Si network with channels of six-membered rings in the direction of the c-axis. The cesium ions are contained in cavities. Certain similarities of the correct unit cell to the incorrect Russian hexagonal and Langlet orthorhombic cells described in earlier reports have been noted.

Small single crystals of CsAlSiO_4 and $\text{CsAlSi}_2\text{O}_6$ have been grown by hydrothermal techniques. The growth conditions were:

Batch: 30 mg of dessicated $\text{Cs}_2\text{O} \cdot \text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2$ gel
0.3 ml CsOH (3M)

Gold Tube: 770°C 11,700 psi 13 days

The habit of CsAlSiO_4 was needles and of $\text{CsAlSi}_2\text{O}_6$, icosahedrons.

Methods have been developed for preparing large (50 g) pure phase batches of CsAlSiO_4 and $\text{CsAlSi}_2\text{O}_6$. The batches were chemically analyzed and are currently in use in phase stability studies.

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