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**Quarterly Progress Report -
Research and Development
Activities - High-Level Waste
Immobilization Program:
January Through March 1979**

J. L. McElroy
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November 1979

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QUARTERLY PROGRESS REPORT
RESEARCH AND DEVELOPMENT ACTIVITIES
HIGH-LEVEL WASTE IMMOBILIZATION PROGRAM:
JANUARY THROUGH MARCH 1979

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SUMMARY

Through the High-Level Waste Immobilization Program, the Pacific Northwest Laboratory is conducting research on the solidification of high-level radioactive waste. A major goal of this program is to develop waste glass compositions and reliable processes for their manufacture. This progress report describes the research and development activities for January through March of 1979.

- The Nuclear Waste Vitrification Project (NWVP) culminated this quarter in the production of two canisters of fully radioactive waste glass. Liquid waste, made from zirconium-clad UO_2 power reactor fuel with an average burnup of 25,000 MWd/MT, was converted to glass by the in-can melting process--thus demonstrating the availability of a method for immobilizing the highest-level waste from the nuclear fuel cycle.
- An intrinsic-gamma melt-level detection system was tested during the NWVP demonstrations. The results showed that if a sufficient number of collimators are used the system will track the melt surface with a precision of 1 in. during the filling of cans with waste glass.
- The two canisters filled in the NWVP are both 8 in. in diameter and contain borosilicate glass of very similar compositions. One canister contains 116 kg of glass that generated 0.38 kW of self-heat when produced; the other contains 145 kg of glass, and generates 1.01 kW. The behavior of these canisters in storage will now be evaluated.
- Spray calcination of simulated Savannah River Plant liquid waste at a rate of 400 L/h was demonstrated in the 36-in.-dia calciner. A calciner furnace with an output of 600 kW and a new high-capacity atomizing nozzle were used.
- An extensive comparative study of alternative waste forms is getting under way. Five waste forms are being compared in the first stage of the study, which is being done with simulated, nonradioactive wastes. The waste forms are: concrete-containing waste calcine, sintered waste glass, glass-ceramic, Synroc B (a crystalline assemblage of titanates), and a well characterized borosilicate waste glass (composition 76-68).
- The results of initial tests indicate that the reaction rate of carbon with water, previously found to be very low, may be increased in a radiation field.

PREVIOUS REPORTS

Previous reports in this series were BNWL-1699, -1741, -1761, -1788, -1809, -1826, -1841, -1871, -1893, -1908, -1932, -1949, -1994, -2070, -2242, -2243, -2264, and PNL-2265-1, -2265-2, -2265-3, -2265-4, -2999-1, -2999-2, -2999-3, and -2999-4.

CONTENTS

SUMMARY	iii
PREVIOUS REPORTS	iv
FIGURES	vii
TABLES	viii
INTRODUCTION	1
SECTION 1. WASTE FORM DEVELOPMENT	3
HIGH-TEMPERATURE GLASS DEVELOPMENT	3
MELTING AND REBOIL STUDY OF SIMULATED WASTE GLASSES	4
RADIATION DAMAGE	5
THERMAL AND MECHANICAL SHOCK	7
CHARACTERIZATION OF ACTUAL HIGH-LEVEL WASTE GLASS CANISTERS	9
Axial Gamma Scans	9
PROCESS CHEMISTRY	11
CFCM-5 Melting Trial	11
Liquid-Fed Ceramic Melter Melting Trial (SRP-11 and SRP-12)	11
PRIMARY STORAGE CANISTER DEVELOPMENT	11
SILICATE-CERAMICS DEVELOPMENT	18
CARBON LEACH TESTING	19
COMPARATIVE STUDIES OF ALTERNATE WASTE FORMS	22
Waste Form Fabrication	22
Cement/PW-9 Calcine	23
PW-9 Sintered-Ceramic	23
Frit/Calcine Sintered-Ceramic	23
76-68 Simulated Waste Glass	23
Celsian Glass-Ceramic	23
Titanate Ceramics	23
Impact Behavior	24
SECTION 2. PROCESS DEVELOPMENT	25
CULMINATION OF THE NUCLEAR WASTE VITRIFICATION PROJECT	25
CALCINE-FED CERAMIC MELTER	28
CERAMIC MELTER DEVELOPMENT	31

IN-CAN MELTING DEVELOPMENT	32
EFFLUENT CONTROL	34
SPRAY CALCINATION OF SAVANNAH RIVER PROJECT LIQUID WASTE	34
Spray Calciner Tests	35
REMOTE LAB-SCALE VITRIFICATION PROGRAM	36
REFERENCES	37

FIGURES

1	Stored Energy, Density, and Diffracted X-Ray Intensity Changes as a Function of Dose in ^{244}Cm -Doped 77-260 Simulated Waste Glass	6
2	Alpha-Autoradiograph and Corresponding Optical Micrographs of ^{244}Cm -Doped 77-260 Simulated Waste Glass	7
3	Particle Sizes Produced by 160 ft-lb Impact on ^{244}Cm -Doped 77-260 Simulated Waste Glass at Two Different Dose Levels	9
4	Axial Gamma Scans of NWVP Canisters	10
5	Grab Sample Analyses from CFCM-5 Melting	12
6	Photomicrograph of Spinel Sludge	13
7	Controlled Water Storage Test Facility	15
8	Twist-Lock Lid for ICM Canister	16
9	Remotely Operable Welder for Sealing Waste Canisters	17
10	Effect of Uranium Additions to Silicate-Ceramic Phases	21
11	Reaction Rate of Graphite Powder in Distilled Water	22
12	Weight-Percent Fines Produced by an Impact of 117 J	24
13	SC/ICM System	26
14	NWVP Waste Canister Before Filling	27
15	BSCM Airlift Detail	32
16	Two Methods of Liquid Feedrate Control	35
17	Spray Calciner Power Consumption	36

TABLES

1	Composition of High-Temperature Waste Glasses	3
2	Leachability of High-Temperature Glasses 79-121 Through 79-126, Existing Waste Glasses, and a Number of Natural and Man-Made Materials	4
3	²⁴⁴ Cm Concentration in Slow-Cooled (-6°C/h) Sample As Determined by Alpha-Autoradiography	7
4	Leach Rates of ²⁴⁴ Cm-Doped 77-260 Simulated Waste Glass	8
5	Analysis of Spinel Sludge Samples	12
6	Liquid-Fed Ceramic Melter SRL-11 Run Grab Sample Analysis	14
7	Unit Cell Parameters for Silicate-Ceramic Phases	20
8	Compositions of Synroc B Constituents and Mixes	24
9	Description of Spent Fuel Used in NWVP	25
10	Operating Conditions, NWVP Runs #1 and #2	28
11	NWVP Canister Data, Runs #1 and #2	28
12	Spray Calciner Process Off-Gas System Decontamination Factors	34
13	Savannah River Liquid Waste Composition Based on 1000 Liters Feed Slurry	34
14	Nozzle Comparisons	35
15	Spray Calciner/In-Can Melter Tests	36

QUARTERLY PROGRESS REPORT
RESEARCH AND DEVELOPMENT ACTIVITIES
HIGH-LEVEL WASTE IMMOBILIZATION PROGRAM:
JANUARY THROUGH MARCH 1979

INTRODUCTION

The High-Level Waste Immobilization Program (HLWIP)--formerly the Waste Fixation Program--is conducted by the Pacific Northwest Laboratory (PNL), operated by Battelle Memorial Institute for the Department of Energy (DOE). Under this program, PNL is conducting research to convert high-level radioactive waste to stable, nondispersible forms. Candidate waste forms include silicate glasses and various crystalline and multibarrier waste forms. The HLWIP is designed to be a means through which the government and users of the technology can cooperate to effectively handle nuclear waste. Objectives of the comprehensive program include: the development and characterization of waste forms; equipment and process development; and design, construction, and demonstration of full-scale process equipment. The following sections describe research and development activities in radioactive waste fixation for the past quarterly reporting period.

SECTION 1. WASTE FORM DEVELOPMENT

The purpose of this task is to develop solidified waste forms for high-level radioactive waste for the commercial fuel cycle and the defense program. The waste forms must have properties that will increase safety, and they must be compatible with all steps of nuclear waste management, including large-scale processing, interim surface storage, transportation, and deep geologic disposal.

HIGH-TEMPERATURE GLASS DEVELOPMENT - G. B. Mellinger and B. O. Barnes

It has been suggested that it may be possible to produce nuclear waste glasses with chemical durabilities superior to those of existing waste glasses by using compositions that require processing temperatures above those currently employed (1050° to 1100°C). A series of glasses was made to test the degree of improvement that could be achieved by making glasses with melting temperatures on the order of 1500°C. The compositions of these glasses are shown in Table 1. The glasses are based on a number of European glasses that have been developed for high chemical durability. Also included was a Pyrex-based composition. All glasses contained 10 wt% PW-4b-(6 & 7).

All of the melts except the one based on Pyrex produced acceptable, well melted, homogeneous glasses. The Pyrex-based glass was not completely reacted and appeared to have a number of phases present. This is understandable, as Pyrex-type glasses need processing

TABLE 1. Compositions of High-Temperature Waste Glasses

Constituent	PNL Designation and Weight Percent					
	79-121 ^(b)	-122 ^(c)	-123 ^(d)	-124 ^(e)	-125 ^(f)	-126 ^(g)
Waste ^(a)	10	10	10	10	10	10
SiO ₂	67.6	63.9	65.0	62.4	66.2	72.9
Al ₂ O ₃	0.5	9.0	1.4	5.4	4.5	1.8
CaO	9.7	3.6	4.6	2.7	5.4	-
Na ₂ O	8.8	0.9	13.5	5.2	14.6	4.1
K ₂ O	3.5	-	0.9	2.6	-	-
CaF ₂	-	6.3	-	-	-	-
MgO	-	5.4	3.2	1.8	3.2	-
Li ₂ O	-	0.9	-	-	-	-
B ₂ O ₃	-	-	1.5	-	-	-
BaO	-	-	-	6.3	-	-
ZnO	-	-	-	3.6	-	-

(a) PW-46-(6 & 7)

(b) Composition # 3/06 (Volf 1961)

(c) Composition # 3/20 (Volf 1961)

(d) Composition # 3/07 (Volf 1961)

(e) Composition # 3/16 (Volf 1961)

(f) Composition # 3/19 (Volf 1961)

(g) Pyrex 77-40

temperatures higher than 1500°C. Table 2 shows the leachabilities of 79-121 through 79-125, as well as those of a number of existing waste glasses with melting temperatures of 1050°C. This table also shows for comparison purposes the Soxhlet leachability measured for fused quartz and a number of natural and man-made materials.

Table 2 shows that a small gain (two- to five-fold) in waste glass Soxhlet durability is obtained by going to high-temperature compositions. The gain in pH-4 durability either is negligible or nonexistent. No claim is made that glasses 79-121 through 79-125 are the best high-temperature waste glasses possible; however, the fact that fused quartz and durable natural minerals are not appreciably better indicates that significant order-of-magnitude decreases in leachability are probably not possible.

TABLE 2. Leachability of High-Temperature Glasses 79-121 Through 79-126, Existing Waste Glasses, and a Number of Natural and Man-Made Materials.

Material	Description	Leach Test, wt% loss	
		pH-4 (19-h)	Soxhlet (24-h)
Quartz Crystals	Natural Material		0.14 ^(a)
Milky Quartz	Natural Material		0.17 ^(a)
Corundum	Natural Material		0.26 ^(a)
Granite	Natural Material		0.37 ^(a)
Basalt	Natural Material		2.03 ^(a)
Pyrex	Commercial Material		0.18 ^(a)
Fused Quartz	Commercial Material	0.05	0.217
76-78	Low-Melting (T = 1050°C) Waste Glass	0.04	1.61
76-183	Low-Melting (T = 1050°C) Waste Glass	0.15	1.38
76-375	Low-Melting (T = 1050°C) Waste Glass	0.61	1.45
79-121	High-Melting (T = 1500°C) Waste Glass	0.19	0.55
79-122	High-Melting (T = 1500°C) Waste Glass	0.18	0.24
79-123	High-Melting (T = 1500°C) Waste Glass	0.13	0.69
79-124	High-Melting (T = 1500°C) Waste Glass	0.19	0.32
79-125	High-Melting (T = 1500°C) Waste Glass	0.18	0.56

(a) Data calculated from 72-h Soxhlet test data. (McElroy 1975)

MELTING AND REBOIL STUDY OF SIMULATED WASTE GLASSES - Dr. L. D. Pye (Alfred University, Alfred, N. Y.)

During this quarter most effort has been directed at personnel hiring, a literature search, and identifying necessary equipment. Three potential controlling mechanisms of melt gas generation are:

1. temperature-dependent gas solubilities
2. gas generation associated with re-dissolution of devitrified phases
3. electrochemical evolution.

The experimental program is intended to identify which of these mechanisms is controlling under specific conditions.

RADIATION DAMAGE - W. J. Weber, R. P. Turcotte, L. R. Bunnell, F. P. Roberts, and J. H. Westsik, Jr.

The experimental investigation of accelerated radiation damage effects in one vitreous and two partially devitrified forms of ^{244}Cm -doped 77-260 simulated waste glass has essentially been completed during the past reporting period. Changes in diffracted x-ray intensity, density, and stored energy have nearly saturated. Final leach and impact tests have been carried out. The radiation dose has reached 5×10^{18} alpha-decays/cm³, which is equivalent to $\sim 10^3$ years' storage of commercially reprocessed wastes (3.3% enriched UO_2 fuel) or more than 10^6 years' storage of defense-type wastes.

The changes in density as a function of accumulated alpha decay are shown in Figure 1. The density change in the vitreous sample is minimal ($\pm 0.1\%$). The density change in the 700°C, one-week annealed sample has saturated at -0.45%. The greatest density change occurs in the slow-cooled sample (-6°C/h); in this sample the density change is slowly approaching a saturation value slightly in excess of -1.0%.

Two major devitrification products are present in both of the partially devitrified samples. The diffracted intensity ratios (I/I_0) for these two phases are shown in Figure 1 as a function of accumulated alpha decay. The results clearly show the amorphization, with respect to x-rays, of the $\text{Ca}_3\text{Gd}_7(\text{SiO}_4)_5(\text{PO}_4)_2$ phase in both sample types; however, the $\text{Gd}_2\text{Ti}_2\text{O}_7$ is relatively resistant to radiation damage. An estimate of the relative ^{244}Cm concentration in the slow-cooled sample was obtained by alpha-autoradiography. An alpha-autoradiograph and corresponding optical micrograph of a typical region are shown in Figure 2. The results of the analysis of relative track densities are given in Table 3.

Microcracking was observed in all slow-cooled samples receiving a dose over 5×10^{17} alpha-decays/cm³. The extent of the microcracking was strongly dependent on dose, local crystal size, and crystal density. The results suggest that the cracking saturates at about the dose level where x-ray amorphization of the $\text{Ca}_3\text{Gd}_7(\text{SiO}_4)_5(\text{PO}_4)_2$ phase is complete. Optical micrographs of identical areas in a typical specimen taken before cracking (2×10^{16} alpha-decays/cm³) and after cracking (8×10^{17} alpha-decays/cm³) are shown in Figures 2b and c, respectively. No microcracking was observed in either the vitreous sample or the 700°C, one-week annealed sample after an accumulated dose of 4.5×10^{18} alpha-decays/cm³. Since water lowers the apparent strength of glass by static fatigue, the samples were also exposed to room-temperature water for three weeks and re-examined in an attempt to more clearly identify stresses around the crystallites. The vitreous sample remained unchanged, the 700°C, one-week annealed sample developed a few cracks, and the slow-cooled sample developed no additional microcracks. Furthermore, no cracks developed in identically prepared specimens of undoped glass exposed to water, confirming that the observed microcracking is a result of radiation-induced stresses associated with x-ray amorphization of the $\text{Ca}_3\text{Gd}_7(\text{SiO}_4)_5(\text{PO}_4)_2$ phase.

Stored energy changes for the three sample types are similar to changes in other waste glasses previously studied--not exceeding 30 cal/g in any of the samples.

FIGURE 1. Stored Energy, Density, and Diffracted X-Ray Intensity Changes as a Function of Dose in ²⁴⁴Cm-Doped 77-260 Simulated Waste Glass

FIGURE 2. Alpha-Autoradiograph and Corresponding Optical Micrographs of ^{244}Cm -Doped 77-260 Simulated Waste Glass

- (a) Alpha-autoradiograph showing ^{244}Cm concentrated in crystals.
 (b) No microcracks in same area after 2×10^{16} alpha-decays/cm³.
 (c) Microfracturing after 8×10^{17} alpha-decays/cm³.

TABLE 3. ^{244}Cm Concentration in Slow-Cooled (-6°C/h) Sample As Determined by Alpha-Autoradiography

Component Phase	^{244}Cm Concentration, wt%
$\text{Ca}_3\text{Gd}_7(\text{SiO}_4)_5(\text{PO}_4)_2\text{O}_2$	6
$\text{Gd}_2\text{Ti}_2\text{O}_7$	4
Residual Glass	1

The leach test results are shown in Table 4. The leach rates based on Soxhlet and static pH-4 and pH-9 tests are not significantly affected by radiation damage. The results also show that the leach rates based on weight loss are, in general, higher than those based on ^{244}Cm -solution analysis. This suggests that the ^{244}Cm is not as readily leached as is the bulk glass.

The impact test results are shown in Figure 3. The data indicate that the samples were marginally better in impact behavior than was soda-lime-silica glass. The results also suggest that the radiation damage did not negatively affect the impact resistance (and, by inference, the strength) of the samples; in fact, in all cases the samples receiving the higher doses appear to be somewhat better. This raises the possibility of some bias in one or the other set of data; this possibility will be given further consideration.

THERMAL AND MECHANICAL SHOCK - L. R. Bunell

An experiment designed to study the effect of devitrification-induced microcracking on the strength of 72-68 glass was completed. Samples of 72-68 glass were prepared in the vitreous form by casting at 1100°C and cooling rapidly to 500°C , from which temperature they were cooled slowly. Devitrified samples were prepared as above, but were heated for 432 h at 900°C . Samples were prepared for the splitting tensile test by core-drilling; this procedure worked well for the vitreous specimens, but the devitrified ones were so severely cracked that

TABLE 4. Leach Rates of ^{244}Cm -Doped 77-260 Simulated Waste Glass

Waste Glass Condition	Leach Rate Based on Weight Loss, g/cm ² -d			Leach Rate Based on ^{244}Cm , g/cm ² -d		
	Soxhlet	pH-4	pH-9	Soxhlet	pH-4	pH-9
<u>Vitreous</u>						
3.5×10^{17} alpha-decays/cm ³	3.0×10^{-4}	1.2×10^{-14}	7.4×10^{-5}	9.5×10^{-7}	7.5×10^{-5}	9.6×10^{-8}
2.3×10^{18} alpha-decays/cm ³	3.0×10^{-4}	1.2×10^{-4}	3.4×10^{-5}	5.1×10^{-7}	1.2×10^{-4}	4.2×10^{-9}
4.4×10^{18} alpha-decays/cm ³	2.7×10^{-4}	7.2×10^{-5}	8.5×10^{-6}	7.9×10^{-7}	2.0×10^{-4}	9.6×10^{-9}
<u>Devitrified (700°C, 1 week)</u>						
3.5×10^{17} alpha-decays/cm ³	1.8×10^{-4}	2.0×10^{-4}	1.7×10^{-5}	1.0×10^{-6}	4.4×10^{-4}	5.7×10^{-8}
2.3×10^{18} alpha-decays/cm ³	2.0×10^{-4}	2.8×10^{-4}	8.4×10^{-6}	2.5×10^{-6}	4.0×10^{-4}	5.2×10^{-9}
4.4×10^{18} alpha-decays/cm ³	1.2×10^{-4}	2.1×10^{-4}	6.7×10^{-5}	8.1×10^{-7}	1.4×10^{-4}	2.4×10^{-8}
<u>Devitrified (-6°C/h)</u>						
3.5×10^{17} alpha-decays/cm ³	6.0×10^{-4}	(a)	(a)	3.7×10^{-6}	(a)	(a)
2.3×10^{18} alpha-decays/cm ³	5.4×10^{-4}	(a)	(a)	2.3×10^{-6}	(a)	(a)
4.4×10^{18} alpha-decays/cm ³	5.7×10^{-4}	(a)	(a)	9.9×10^{-7}	(a)	(a)

(a) Samples unavailable for testing.

FIGURE 3. Particle Sizes Produced by 160 ft-lb Impact on ^{244}Cm -Doped 77-260 Simulated Waste Glass at Two Different Dose Levels (a)

(a) Results are compared to undoped soda-lime-silica glass.

only a very few samples could be obtained. In all, 29 vitreous and 5 devitrified specimens were tested. The strength of the vitreous specimens was 4858 psi, with a standard deviation of 748 psi; corresponding values for the devitrified material were 1660 psi and 477 psi, respectively. There is no statistical difference between the variance of the two sets of data. Application of the "T" test showed very positive confidence that the two average strengths are different.

CHARACTERIZATION OF ACTUAL HIGH-LEVEL WASTE GLASS CANISTERS - W. L. Kuhn

Two canisters of radioactive borosilicate glass were produced this quarter by the Nuclear Waste Vitrification Project (NWVP). These canisters are now being characterized with respect to external physical dimensions and properties, and thermal and radiation characteristics. Upon completion of nondestructive examination and the welding of lids onto both canisters, one canister will be committed to destructive sampling to provide glass specimens for further detailed analyses. The other will be stored in its pristine condition.

Axial Gamma Scans

Both canisters have been scanned for homogeneity of gamma radiation emanation. Counts were taken every 6 in. along the canisters' lengths, beginning at the top of the glass fill; some additional counting was done near the top and bottom of each.

Results from the scans are plotted in Figure 4 for the two canisters (#1 and #2) for ^{137}Cs , ^{154}Eu and ^{106}Ru (^{106}Rh). The fill height in canister #1 is about 54 in., and for canister #2 about 66 inches. The ^{106}Ru results are the least precise because of the low count rate. Note the separate scales for ^{137}Cs and $^{154}\text{Eu}/^{106}\text{Ru}$.

The results for ^{137}Cs show excellent uniformity except at the bottom of canister #2 (66 in. below top of fill), where the peak corresponds to a calcine-rich layer known to have been inadvertently created by a holdup in frit flow. The same peak is seen for ^{154}Eu and ^{106}Ru . The low ^{137}Cs activity about 6 in. below top of fill for both canisters is probably due to a frit "cap" finishing off the vitrification runs; the higher counts at the top are possibly a result of calcine falling belatedly from inside surfaces of the calciner equipment and connections, after the frit "cap" is complete. This count distribution is not quite the same for ^{154}Eu --or especially for ^{106}Ru , which shows a count peak in the assumed frit-rich region. Except at the very top and bottom, the ^{154}Eu distribution is uniform. It is not yet known if the variation in the ^{106}Ru counts are statistically significant.

FIGURE 4. Axial Gamma Scans of NWVP Canisters

PROCESS CHEMISTRY - J. M. Lukacs and C. C. Church

CFCM-5 Melting Trial

From 9/19/79 to 9/28/79 the calcine-fed ceramic melter (CFCM) produced over 9000 kg of simulated SRP Composite-411 glass. Grab samples periodically collected during the run were analyzed chemically and by x-ray diffraction. Figure 5 plots this information, as well as the annealed glass density. Nominally, the glass product was close to the target composition. Some fluctuation is apparent in density and composition; however, the source was not identified. No crystalline material was detected in any glass sample.

Following the run, operating personnel detected a viscous layer on the melter floor. Samples taken identified it as a spinel (NiFe_2O_4 -type) crystal accumulation. Subsequent draining operations removed all glass from the CFCM. A viscous layer 4 to 6 in. thick remained on the floor. The green lower third of this material was rich in CeO_2 and was a remnant of an earlier melter run with high-fission-product glass. The black upper two-thirds contained approximately 30 wt% of spinel crystals in a divitrified glass matrix. At process temperatures only spinel crystals would be present. Table 5 presents both the x-ray diffraction and chemical analysis results for two spinel sludge samples. Figure 6 shows a typical micrograph for this material, with the spinel appearing as bright angular crystals. In relation to the total quantity of waste glass produced, the amount of Fe, Mn and Ni remaining is quite small. If all of the Fe, Mn and Ni in the spinel sludge was gradually removed from the waste glass during the run, the concentrations of Fe_2O_3 , MnO_2 and NiO in the glass product would be reduced by 0.4%, 0.1% and 0.05%, respectively. Without an accurate fix on waste feed consistency it would be difficult to confirm crystal segregation solely by waste glass analysis. Additional sludge analysis work is ongoing.

Liquid-Fed Ceramic Melter Melting Trial (SRP-11 and SRP-12)

The SRP Composite-411 glass composition was produced in the (LFCM) in December 1978. In a manner similar to that used for the CFCM-5 trial, grab samples were analyzed to determine melter response to a major composition change. Table 6 presents these data.

The last product sample taken on 12/5/78 was close to the target Composite-411 composition. Samples taken from the LFCM during operation did not indicate a major spinel accumulation, as had occurred in the CFCM.

PRIMARY STORAGE CANISTER DEVELOPMENT - S. C. Slate

We started an important series of long-term tests this quarter to demonstrate the performance of primary canisters in interim water storage. High-level wastes that generate heat may need to be stored in controlled water basins for periods of up to ten years. Our tests will provide data on the corrosion performance of prototypic waste canisters under various water basin conditions.

We are testing three 12-in.-dia 304L canisters that were filled in a prototypic manner by the in-can melting (ICM) process. The canisters are placed in 2-ft-dia test pods in which we simulate the conditions found in water storage basins. The water is circulated past the canister and is heated. The water chemistry and temperature will range from ideal to worst-case conditions. Ten other pods will be started at a later date to test additional canisters. Figure 7 shows one of the test canisters being lowered into a test pod.

FIGURE 5. Grab Sample Analyses from CFCM-5 Melting

TABLE 5. Analysis of Spinel Sludge Samples

		Sludge #2, wt%	Sludge #6, wt%	SRP Comp.- 411, wt%
X-Ray	NiFe ₂ O ₄ spinel	28	30	(a)
	NaAlSiO ₄	18	17	(a)
	Unidentified crystal phases	<u>12</u>	<u>8</u>	<u>(a)</u>
	Total estimated crystallinity	58	55	
Chemical Analysis	Na ₂ O	8.47	7.50	9.4
	Li ₂ O	5.78	4.59	9.4
	SiO ₂	26.3	24.7	44.5
	Al ₂ O ₃	18.7	16.8	12.0
	MnO ₂	6.43	7.12	2.6
	Fe ₂ O ₃	26.1	29.2	8.0
	NiO	2.97	3.46	0.6
	CaO	<u>3.04</u>	<u>2.57</u>	<u>5.2</u>
		97.79	95.94	91.7

(a) Not available.

50X

250X

8.3X

FIGURE 6. Photomicrograph of Spinel Sludge

Before the canisters were placed in these test pods they were seal-welded using a remotely operable welder. This welder was designed and built especially to make the seal weld on the PNL twist-lock closure design, which is the reference design for ICM canisters. The twist-lock lid and the welder are shown in Figures 8 and 9. The twist-lock lid has been discussed in detail in two PNL documents (Simonen, Griffiths and Thurgood 1978; Simonen and Slate 1979).

TABLE 6. Liquid-Fed Ceramic Melter SRL-11 Run Grab Sample Analysis

Date	Time	Annealed Density, g/cc	Produced, kg(a)	Oxides Detected, wt%									
				Na ₂ O	Li ₂ O	CaO	SiO ₂	Al ₂ O ₃	MnO ₂	Fe ₂ O ₃	NiO	ZnO	MoO
12/10/78	2005	2.647 $\pm$ 0.031 ^(b)	50	9.0	0.4	5.2	45.7	4.2	0.1	0.6	0.2	5.8	1.2
12/10/78	2300	2.706 $\pm$ 0.006	255	11.1	0.4	5.4	47.3	4.4	0.1	0.6	0.2	5.6	1.3
12/11/78	0205	2.660 $\pm$ 0.011 ^(b)	449	11.5	0.4	5.1	49.0	4.5	0.1	0.6	0.2	5.2	1.3
12/11/78	0600	2.692 $\pm$ 0.001	672	10.4	0.7	5.5	48.2	6.9	0.1	0.9	0.2	4.5	1.1
12/11/78	0900	2.608 $\pm$ 0.005 ^(c)	926	7.7	4.4	5.9	50.0	6.0	1.2	3.8	0.3	0.3	0.1
12/11/78	1300	2.612 $\pm$ 0.003	1085	8.4	5.4	5.7	48.3	7.0	1.5	4.6	0.3	0.3	0.1
12/11/78	1900	2.618 $\pm$ 0.008	1363	8.4	6.2	5.8	49.0	8.0	1.6	5.3	0.4	0.2	0.1
12/12/78	0300	2.602 $\pm$ 0.013 ^(b)	1678	9.6	6.0	5.5	46.1	8.4	1.9	5.7	0.4	0.3	0.1
12/12/78	1755	2.631 $\pm$ 0.008	2215	8.4	7.2	5.3	47.0	10.6	2.2	6.5	0.5	0.1	0.1
12/13/78	1145	2.638 $\pm$ 0.013	2816	8.9	7.8	5.2	45.5	10.2	2.4	7.0	0.5	0.1	0.1
12/14/78	0435	2.631 $\pm$ 0.012	3470	8.5	8.4	4.9	46.3	11.1	2.4	7.1	0.5	0.4	0.1
12/14/78	2200	2.639 $\pm$ 0.003	4190	9.7	8.9	4.9	43.5	11.4	2.6	7.6	0.6	0.1	0.1
12/15/78	1300	2.642 $\pm$ 0.001	4766	9.7	9.0	5.0	43.9	11.2	2.6	7.6	0.6	0.1	0.1
SRP Composite-411				9.4	9.4	5.2	44.5	12.0	2.6	8.0	0.6	0	0

(a) SRP-11 run started on 12/10/78 at 1925 hours.

(b) Some porosity.

(c) Color changed from green to brown for all subsequent samples.

FIGURE 7. Controlled Water Storage Test Facility

FIGURE 8. Twist-Lock Lid for ICM Canister

FIGURE 9. Remotely Operable Welder for Sealing Waste Canisters

The welder uses the gas-tungsten process to make an autogenous fillet weld that can range from 1/8 to 1/4 in. thick. The welder is positioned off a hole in the canister lid. By maintaining tight tolerances on the lid itself we eliminate any need for automatic tracking of the torch or for voltage controls.

Operation of this welder is quite simple. The lid is tack-welded in four locations and the automatic welding sequence is initiated. The welding sequence rotates heat around the lid, making the weld. When the weld is completed the welder decreases the current and then stops. We expect that a simple procedure can be followed to make high-quality, reproducible welds.

Cooling of the welding torch is done passively by the cover gas and a small finned heat pipe. Very few parts on the device will require maintenance. However, those parts that do require routine maintenance are easily replaced. Also, total cost for the in-cell portion of this unit is quite low, making replacement a reasonable alternative to repair.

Several special features were included on the device to improve its remote operation. No organic parts were used except for one O-ring on a cable and the motor insulation, and both of these parts are easily replaced. During operation only the torch rotates, so the supply cables do not twist. The welding current supply and ground paths were made part of the structure. The welding current passes through gold plating on the support arm to the torch and the ground contact is made through the bottom of the welder to the lid, so no additional connections to the canister are required.

We performed a helium-leak inspection of the seal-welds on the three canisters by placing a stainless bell jar over the weld and drawing a vacuum for 15 minutes. The canister was pressurized to 15 psig with helium. The canisters were all tested to a level of about 5×10^{-9} at m-cc/sec.

SILICATE-CERAMICS DEVELOPMENT - J. M. Rusin, G. J. McCarthy (Pennsylvania State University, University Park, PA)

All of the constituents of Thorex wastes, except fluorine, can be accommodated in existing silicate-ceramic mineral models and processed by the usual PNL calciner/disc-pelletizer technology. During this processing, much of the fluorine would appear in the off gas. However, it is possible that if a closed system technique such as hot isostatic pressing were used, fluorine might crystallize in the apatite-structure solid-solution phase. Research has continued to see if modified synthetic mineral models would provide a sufficiently refractory fluorine-containing phase.

Fluorapatite [$\text{Ca}_{10}(\text{PO}_4)_6\text{F}_2$, a common fluorine phase in nature,] was examined for ease of synthesis and thermal stability at scouting silicate-ceramic crystallization-consolidation temperatures (i.e., 1100° to 1200°C). It was found that fluorapatite could be readily synthesized by the usual calcination-of-liquids route. In fact, this phase was already crystalline after the 600°C calcination, and higher-temperature firings of up to 1000°C increased crystallinity. X-ray diffraction studies of the products from firing the calcine at 800° to 1200°C in air indicated no decomposition during 2-h firings at up to 1000°C, and during 6-h firings at up to 900°C. Chemical analyses of each product for fluorine

concentration indicated that the 1100° and 1200°C firings did cause fluorine losses of ~20 wt% and ~16 wt%, respectively. Thus, fluorapatite may not be satisfactory for F-fixation, as processing temperatures of 1100° to 1200°C are usually required to obtain a low-porosity product.

As the first step in quantitative x-ray phase analysis of existing silicate-ceramics, it was necessary to determine the unit cell parameters for each of the major phases. Obtaining precision data from these 8- to 10-phase ceramics is quite difficult because of the many coincidental and overlapping reflections. However, enough unambiguously indexed reflections were found to derive the data listed in Table 7 by the usual computer refinement methods. The standard errors in the last digit, reported in parentheses [e.g., 5.311(4) = 5.311 ± 0.004] are also given.

Quantitative x-ray phase analysis of existing silicate-ceramics is not that straightforward. Most of the phases occurring in crystallized silicate-ceramics do not have the relatively simple stoichiometries specified in the phase formation models. Substitution of minor elements and partitioning of major elements among several phases is to be expected. As the microchemistry of each of these phases is determined, the crystal chemistry of any unusual solid-solution substitutions will be examined. In this way one can model, and in many cases verify the stability of, particular phases in these complex silicate-ceramics. The synthesized phases will then be used as standards for the quantitative x-ray phase analyses.

Because of restrictions placed upon the use of uranium in the full-scale PNL calciner, the silicate-ceramic calcine does not contain uranium, and cerium is often used as a substitute. The effect of uranium on the formation of the proposed silicate-ceramic phases was studied by adding uranyl nitrate to the calcined powder. The exact phase(s) containing uranium have not been determined, although uranium was not detected in the apatite phase.

Through the use of information contained in Table 7, one can get an indication of the effect of uranium additions. This can be done by comparing unit cell parameters for the silicate-ceramic phases with and without uranium additions; such a comparison is shown in Figure 10. The data suggest that uranium additions do have measurable effects upon the silicate-ceramic phases. In SPC-2, the apatite phase is greatly affected, resulting in a 10.85% increase in the co-lattice constant. There is a corresponding volume increase from 556.2 Å³ to 607.2 Å³, which represents an increase of 9%. In SPC-4, the fluorite phase is the main phase affected. These results still do not indicate where the uranium directly appears, as it may just cause other elements to shift compositions.

CARBON LEACH TESTING - W. J. Gray

Carbon is expected to have a very low leach (oxidation) rate, and is therefore attractive as one of the barriers of a multibarrier waste form. Tests to determine the leach rate of carbon are in progress.

Work reported last quarter (McElroy et al. 1979) has been expanded to include tests in an autoclave and in a gamma-irradiation facility. Experimental procedures and computation methods were essentially the same as reported earlier.

Autoclave results at 200° and 300°C are shown in Figure 11 as an extension of data reported last quarter at lower temperatures. The point at 300°C falls below the line because the oxygen was almost entirely depleted from the reaction vessel. This supports the suggestion

TABLE 7. Unit Cell Parameters^(a) for Silicate-Ceramic Phases

	Solid Solution Structure Type				
	Apatite (hexagonal P6 ₃ /m) A _{SS}	Scheelite (tetragonal I4 ₁ /a) S _{SS}	Monazite (monoclinic P2 ₁ /n) M _{SS}	Fluorite (cubic Fm3m) F _{SS}	Polylucite (cubic Ia3d) P
SPC-2 PNL spray calcine; pelletized and fired at 1200°C in air for 2 h at PSU	a ₀ = 9.556(4) c ₀ = 7.032(16) v = 556.2	a ₀ = 5.307(6) c ₀ = 11.820(12) v = 332.9	a ₀ = 6.808(8) b ₀ = 7.019(8) c ₀ = 6.479(8) β = 103.05(10) v = 301.6	a ₀ = 5.342(3) v = 152.4	a ₀ = 13.640(4) v = 2537
SPC-2 DISC PELLETS Prepared at PNL; crystallization-consolidation at 1110°C for 8 h	a ₀ = 9.524(4) c ₀ = 7.001(8) v = 549.9	a ₀ = 5.311(4) c ₀ = 11.801(12) v = 332.9	a ₀ = 6.788(8) b ₀ = 7.023(4) c ₀ = 6.469(6) β = 103.74(10) v = 299.7	a ₀ = 5.358(4) v = 153.9	a ₀ = 13.636(4) v = 2535
SPC-2+U Prepared at PSU from PNL spray calcine + U nitrate; fired at 1200°C for 2 h	a ₀ = 9.484(4) c ₀ = 7.795(8) v = 607.2	a ₀ = 5.312(3) c ₀ = 11.824(6) v = 333.7	a ₀ = 6.806(4) b ₀ = 6.910(6) c ₀ = 6.323(4) β = 103.21(10) v = 289.5	a ₀ = 5.384(3) v = 156.1	a ₀ = 13.646(4) v = 2541
PSU-SPC-2+U Complete batch prepared at PSU by boil-down procedure; fired at 1200°C for 2 h	a ₀ = 9.480(4) c ₀ = 6.957(8) v = 541.5	a ₀ = 5.300(8) c ₀ = 11.851(8) v = 332.9	a ₀ = 6.750(8) b ₀ = 6.998(8) c ₀ = 6.433(8) β = 103.98(10) v = 294.9	a ₀ = 5.339(3) v = 152.2	a ₀ = 13.639(4) v = 2537
SPC-4 PNL spray calcine; pelletized and fired at 1200°C for 2 h at PSU	a ₀ = 9.505(4) c ₀ = 6.978(4) v = 546.0	a ₀ = 5.382(4) c ₀ = 11.971(4) v = 346.8	a ₀ = 6.750(4) b ₀ = 6.968(4) c ₀ = 6.409(4) β = 103.47(6) v = 293.2	a ₀ = 5.192(3) v = 140.0	a ₀ = 13.645(4) v = 2540
SPC-4 DISC PELLETS Prepared at PNL; crystallization-consolidation at 1230°C for 4 to 8 h	a ₀ = 9.497(4) c ₀ = 6.976(4) v = 544.9	a ₀ = 5.378(4) c ₀ = 11.999(8) v = 347.1	a ₀ = 6.749(4) b ₀ = 6.971(4) c ₀ = 6.432(4) β = 103.96(10) v = 293.7	a ₀ = 5.190(3) v = 139.8	a ₀ = 13.649(6) v = 2542
SPC-4+U Prepared at PSU from PNL spray calcine + U nitrate; fired at 1200°C for 2 h	a ₀ = 9.505(4) c ₀ = 6.975(4) v = 545.9	a ₀ = 5.378(3) c ₀ = 11.933(6) v = 345.2	a ₀ = 6.759(8) b ₀ = 6.951(10) c ₀ = 6.439(10) β = 103.72(10) v = 293.9	a ₀ = 5.347(3) v = 152.9	a ₀ = 13.649(6) v = 2542

(a) a₀, b₀, c₀ in Å; β in degrees; v in Å³.

FIGURE 10. Effect of Uranium Additions to Silicate-Ceramic Phases

made last quarter that the graphite reacted with oxygen rather than with the water. Additional experiments have begun to examine radiolysis effects, which are known to contribute significantly to the reaction between water vapor and graphite at lower temperatures where the thermal reaction rate is low. Just one test has been made so far in a gamma-irradiation facility. A total dose at 32°C of 1.4×10^7 roentgens was accumulated in 24 h using a ^{60}Co source. This produced a reaction rate of 1.3×10^{-7} g/cm²-d. In the absence of a radiation field, the reaction rate at 32°C is too low to be measurable (i.e., less than about 4×10^{-11} g/cm²-d). This test also produced considerable hydrogen--about three times more H₂ than CO₂. In all other tests, the amount of H₂ has been no more than 2% of the CO₂ concentration. The presence of H₂ may imply that in this case the graphite reacted with water, rather than with oxygen as in the other tests, but additional work is required to confirm this.

Reaction rate tests in oxygen-free systems (simulating deep geologic conditions) are in progress in an effort to study the reaction with water. There are also plans to investigate the possibility that the reactions in systems containing air are somehow catalyzed, since the activation energy estimated from the data in Figure 11 is significantly lower than expected.

FIGURE 11. Reaction Rate of Graphite Powder in Distilled Water^(a)

(a) Average over 24 h.

COMPARATIVE STUDIES OF ALTERNATE WASTE FORMS - R. O. Lokken, R. A. Wheeler, K. R. Welsch

Waste Form Fabrication

Five waste forms have either already been produced or production is in progress. These include 10-wt% PW-9 calcine in Type-II Portland cement, sintered PW-9 calcine with 50 wt% glass frit, celsian glass-ceramic containing 20 wt% PW-9 calcine, and 76-68 simulated waste glass. In addition, Synroc B waste forms have been produced by sintering and hot-pressing.

Cement/PW-9 Calcine

Cement/calcine composite samples were prepared by dry-blending 585 g of Type-II Portland cement with 65 g PW-9 calcine to form a homogeneous mixture. Water was then added ($H_2O/solids = 0.34$) until a consistent paste was attained.

After seven days, 30 samples were core-drilled and sawed to a length of ~ 0.5 inch. The cores revealed some voids created by entrapped air bubbles. The average bulk density of the 30 samples is $1.71 \pm 0.1 \text{ g/cm}^3$. Null pycnometer measurements made on 10 samples showed an average density of $2.6 \pm 0.2 \text{ g/cm}^3$.

PW-9 Sintered-Ceramic

Pellets of PW-9 calcine were prepared by cold-pressing at ~ 7800 psi. The pellets were sintered at 975°C for 2 h after heating at a rate of 200°C/h ; cooling was also done at 200°C/h . Substantial shrinkage occurred during sintering that resulted in a 91.4% density increase to $3.6 \pm 0.1 \text{ g/cm}^3$.

Frit/Calcine Sintered-Ceramic

Thirty-one pellets of 50-wt% PW-9 calcine powder and 50-wt% glass frit were prepared by cold-pressing at ~ 7800 psi of $1.77 \pm 0.02 \text{ g/cm}^3$. The pellets were sintered at 750°C for 2 h; heating and cooling rates were 200°C/h . An increase in density of 24.9% resulted from sintering, yielding an average sintered density of $2.21 \pm 0.02 \text{ g/cm}^3$. The average weight loss was 9.6%.

76-68 Simulated Waste Glass

Pieces of 76-68 simulated waste glass were melted for 2 h in a platinum crucible at $\sim 1050^\circ\text{C}$ and cast into pre-heated graphite molds. The glass was then annealed at 500°C , allowed to furnace-cool, and core-drilled. The average bulk density of the cores was $2.93 \pm 0.01 \text{ g/cm}^3$.

Celsian Glass-Ceramic

Glass-ceramics (De et al. 1976) are produced by crystallization of vitreous forms through special heat treatments. The modified celsian composition in the present work is 80 wt% frit and 20 wt% PW-9 calcine. It is melted at 1200°C , annealed at 550°C for 2 h, heat-treated for 3 h at 600°C and 12 h at 800°C , then annealed for 2-1/2 h at 500°C .

Titanate Ceramics

Synroc, coined from "synthetic rock," (Ringwood et al. 1979) is engineered to incorporate radioactive waste elements in thermodynamically stable, host mineral phases; this is similar to the supercalcine approach. Synroc B consists of three host phases: "hollandite" ($BaAl_2Ti_6O_{16}$), perovskite ($CaTiO_3$), and zirconolite ($CaZrTi_2O_7$). These phases are synthesized by solid-state reactions of oxides at $\sim 1300^\circ\text{C}$. The oxide compositions of the samples fabricated to date are listed in Table 8. Each has been fabricated by sintering and hot-pressing. Sintering proved inadequate because of large amounts of porosity and unreacted species, even though the samples were held at 1350°C for 2 h. Hot-pressing provided samples with greater than 90% densities, but because of low temperatures reactions were again incomplete. Additional heat-treating/crystallization studies are in progress.

TABLE 8. Compositions of Synroc B Constituents and Mixes

Oxide	Synroc B Constituents, wt%				Synroc B Mixes, wt%		
	Hollandite I	Hollandite II	Perovskite	Zirconolite	Synroc Mix (a)	Synroc PW-4	Synroc PW-9
TiO ₂	65.30	74.92	58.81	47.22	57.0	51.3	51.3
ZrO ₂				36.25	11.0	9.9	9.9
Al ₂ O ₃	13.85	13.63			10.0	9.0	9.0
CaO			41.19	16.53	13.0	11.7	11.7
BaO	20.85	11.45			9.0	8.1	8.0
PW-4b-1						10.0	
PW-9							10.0

(a) Reference mix.

Impact Behavior

Six samples each of 76-68 simulated waste glass, PW-9 calcine sintered-ceramic, PW-9/frit sintered-ceramic, and PW-9/cement were impacted with an impact energy of 160 ft-lb (117 J). The particle size distribution of the impacted samples has been determined by weighing sieve fractions. Figure 12 shows the weight-percent fines (<38 μ m) produced by an impact energy of 160 ft-lb. As seen in the figure, the calcine-cement waste form demonstrates the best impact resistance because of its low waste loading. Increasing the waste loading will decrease the overall strength of the composite, and a corresponding decrease in impact resistance is expected. This phenomenon is being studied under a separate experiment and will be reported in future reports.

FIGURE 12. Weight-Percent Fines Produced by an Impact of 117 J

SECTION 2. PROCESS DEVELOPMENT

The purpose of this task is to develop or improve processes for converting liquid high-level radioactive waste into the candidate waste forms that are developed in Task 1. Processes for producing glass as a first-generation waste form are well along in their development; process improvements are still being made, however. Processes for other waste forms must be developed through the sequence of conceptual equipment design, construction, pilot-plant testing, and process integration and demonstration.

CULMINATION OF THE NUCLEAR WASTE VITRIFICATION PROJECT - W. J. Bjorklund, M. S. Hanson, L. K. Holton, L. S. Romero and D. H. Siemens

Two canisters of vitrified HLW from the processing of light water reactor (LWR) fuel were produced in our radiochemical engineering cells this quarter. Actual liquid waste recovered from pressurized water reactor (PWR) fuel was immobilized as a borosilicate glass product in two 8-in.-dia stainless steel canisters. To prepare liquid waste for the immobilization demonstration, six zircaloy-clad PWR fuel elements from the Point Beach Nuclear Power Plant of the Wisconsin Electric Power Company were chopped and dissolved. The fuel is described in Table 9. Uranium and plutonium were removed from the liquid waste by solvent extraction. The two canisters of waste glass produced by vitrification of the liquid HLW represent the culmination of the DOE-sponsored Nuclear Waste Vitrification Project (NWVP), which began in mid-CY-1976. This demonstration is a verification of the technology now in hand for the immobilization of radioactive wastes and demonstrates the capability of the PNL facility to conduct further waste vitrification demonstrations.

The vitrification demonstration was carried out in the PNL-developed spray calciner/in-can melter Process (SC/ICM) (Bonner et al. 1976; Blair 1976) as shown on Figure 13. Liquid waste was pumped from an agitated feed tank and metered to the spray calciner. The calcine powder fell into an 8-ft-long x 8-in.-dia 304L stainless steel canister connected to the bottom of the calciner; Figure 14 shows one such canister. Continuous addition of glass formers was metered proportionally into the canister with the calcine powder. The canister was held at 1000° to 1050°C throughout the process to melt the material into its stable vitreous final form as a borosilicate glass. These canisters will be characterized in ongoing DOE studies at PNL. Technical data summarizing the processing campaigns is shown in Tables 10 and 11.

TABLE 9. Description of Spent Fuel Used in NWVP

Fuel types (A and B)	Point Beach PWR 14 x 14 (179 rods)
Discharge dates	- A October 1972 - B May 1974
Burnups	- A 20,500 MWd/tU - B 29,500 MWd/tU
Initial enrichments	- A 2.27 wt% ²³⁵ U, 398.1 kgU/bundle - B 3.04 wt% ²³⁵ U, 389.2 kgU/bundle
Final enrichments	- A 0.85 wt% ²³⁵ U, 386.6 kgU/bundle - B 0.94 wt% ²³⁵ U, 272.7 kgU/bundle

FIGURE 13. SC/ICM System

FIGURE 14. NWVP Waste Canister Before Filling

TABLE 10. Operating Conditions, NWVP Runs #1 and #2

Parameters and Units	Run #1	Run #2
Feed concentration ^(a) , L/MTU	833	760
Feed acidity, M	4.4	6.6
Solids content, g oxide/L	66	86
Feed processed, L	806	430
Average feed rate, L/h	15.7	12.7
Heat content, w/L	1.12	2.05
Activity, Ci/L	313	526
Run time, hours	53	33.6
Average burnup (fuel), MWD/MTU	20,400	25,900
On stream factor, %	99	96

(a) PW-8a type

TABLE 11. NWVP Canister Data, Runs #1 and #2

Characteristics and Units	Canister Data	
	Run #1	Run #2
Glass weight, kg	116	145
Glass volume, L	41.3	52.9
Fill height, ft	4.5	5.75
Frit-to-calcine ratio, (by weight)	4.2:1	2.2:1
Glass density, g/cc	2.8	2.7
Equivalent uranium, MTU	0.40	0.715
Decay heat, ^(a) watts	380	1012
Activity, ^(a) Ci	1.05×10^5	2.64×10^5

(a) At time of filling.

CALCINE-FED CERAMIC MELTER - R. D. Dierks

The analysis of the observations and data obtained from the combined full-scale spray calciner and calcine-fed ceramic melter (CFCM) systems during ten days of continuous glass production in late September 1978 has been completed. In addition, the CFCM system has been shut down, inspected, modified, reassembled, and, at the end of the report period, is ready to be restarted to undergo a second ten days of continuous glass production and observation.

The combined spray calciner and ceramic melter systems were operated continuously for ten days, starting at a glass production rate of 20 kg/h and ending at a rate of 50 kg/h. The elapsed time for the experiment was 227 h, which included downtime totaling 13.4 hours. Approximately 9040 kg of glass was produced during the experiment.

The calciner feed for this experiment was a simulated Savannah River Plant (SRP) composite sludge slurry containing 0.0617 kg of oxides per liter, and the glass former was Frit 411. The target frit-to-oxides ratio was 3:1 by weight, and for the first 135 h the ratio averaged 3.8:1; for the last 192 h it averaged 2.94:1.

During the 227 h of the experiment, the feed to the calciner/melter system was shut down 21 times for a total downtime of 13.4 h (6% of the total elapsed time). The most frequent failure (12 times, for a total downtime of 2.8 h) was the plugging of the 4-in. flexible pipe that connected the calciner to the melter. This was caused by premature melting of the frit in the 4-in.-dia Inconel sleeve that penetrated the insulation on the underside of the melter cavity lid. At low feed rates this sleeve ran about 800° to 900°C at its lower end, causing the frit to stick to the sleeve and accumulate until the sleeve bridged over and blocked the flow of calcine and frit to the melter. An instrument system monitoring the differential pressure between the calciner and the melter very clearly indicated the accumulation of material in the sleeve and its eventual closure. Plugging of the feed slurry line to the calciner resulted in 2.6 h of downtime, two calciner nozzle changes used up 2.0 h, and an off-gas plugging problem required 6.0 h to correct.

With the exception of the first few hours of the experiment, when some foaming of the glass melt was encountered, the operation of the melter and the appearance of the melter cold cap was stable throughout the experiment. Although the melter gave every indication that it would sustain a higher production rate, it did appear that increasing the feed rate above 50 kg/h might have caused the conical frit pile that accumulates under the feed inlet nozzle to grow in height and block off the bottom of the feed inlet sleeve. Such a blockage would prevent melter off gases from leaving the melter, and prevent calcine and frit from entering the melter.

Each of the massive melter electrodes (28 in. wide x 24 in. high x 2 in. thick) has a 1/2-in.² cross section, serpentine channel designed into the back side of the slab to permit direct cooling of electrodes. At 15 psig inlet pressure, 17 SCFM of cooling air removed 5.4 kW of heat from each electrode. This permitted the input power level to be increased by 18 kW and the electrode current density to be increased from 1.7 to 2.2 amps/in.². The increased power input enabled the melting rate to be increased, or the bulk glass temperature to be increased, without increasing the operating temperature of the electrodes.

Later visual examination of the electrodes did not show any bulging of the cooling channel cover plates, nor any warping or distortion of the electrode slabs over what had resulted from the original welding of the cooling channel cover plates.

On October 23, 1978 the CFCM was drained of its molten glass through a freeze-type bottom drain valve in order to test the operation of the controllable freeze valve and to allow for melter modifications. During normal operation, ~26 SCFM of cooling air flowing continuously through passages in the freeze valve maintained the maximum temperature of the freeze valve nozzle below 400°C, thus keeping a plug of frozen glass in the nozzle. By turning off the cooling air and applying 3 kW of power to two flat-plate electrical heaters positioned on either side of the freeze valve nozzle, the nozzle temperature was raised to 750°C and glass began to flow from the valve, reaching a peak flow rate of 133 kg/h. By applying cooling air or heat, the glass flow through the freeze valve could be throttled, stopped, or restarted at will.

Following the shutdown and cooling of the CFCM, the melter cavity lid was removed and approximately 250 kg of sludge was removed from the melter tank floor. The sludge layer

ranged from 2 in. thick in the center of the tank to about 6 in. thick in the corners. The sludge was found to form two distinct layers: the lower 1/3 was a cerium oxide-glass mixture from initial startup experiments; the upper 2/3 was an iron-rich spinel-glass mixture that accumulated during the continuous 10-d experiment. The spinel formation has been postulated as resulting from: 1) a separation of the frit and calcine as they drop into the melter cavity, 2) periods when the bulk glass temperature was below 1050°C, and 3) little if any convection mixing of the glass in the tank.

Inspection of the electrodes revealed very little corrosion. No D.C. imbalance corrosion was noted, and no metal-line corrosion was seen. Some very light vertical grooving of the electrode faces was noted, but it was so slight that it was undetectable from a weight-change measurement (each electrode weighs about 400 pounds). An inspection of the refractories revealed a slight amount of metal-line corrosion (a 1-in.-wide band about 1.16 in. deep on both the east and west melter walls). No refractory corrosion was noted behind the electrodes at the north and south ends of the tank, nor on the floor. Some rounding of refractory corners was noted around the under-flow throat, as was some rounding of the square refractory edges where an ill fit between adjacent refractory blocks left an 1/8-in. or larger gap between the blocks.

Modifications to improve the performance of the melter, or to provide additional data, have been completed and the melter has been reassembled. To eliminate premature melting of the frit in the insulation penetration sleeve, this cylindrical, 4-in.-dia sleeve has been replaced with a 45° conical Inconel sleeve with a minimum 6-in. diameter. To further discourage premature melting of the frit, the portion of the conical sleeve that extends above the melter lid is water-cooled. The 4-in. flexible pipe connecting the calciner cone to the melter inlet nozzle (the conical sleeve) has been replaced with a 6-in. flexible pipe to permit the calcine and frit to drop into the melter unimpeded by the melter off gases that are moving up into the calciner through the same flexible pipe.

The electrodes have been modified by welding a 2-in.-thick "foot" of Inconel to the bottom of each electrode. These "feet" extend across the width of the electrodes, span 6 in. into the melting cavity, and rest flat on the melter floor. It is expected that with a 12-in. glass depth, 30% of the input power will be dissipated in the bottom 2 in. of the tank, with the remainder uniformly distributed throughout the upper 10 in. of the tank. This is expected to result in increased convection in the melter tank, and in more nearly uniform glass temperatures.

The freeze valve has been replaced with a similar valve of a slightly more rugged design; it has a 1-1/2-in.-dia bore instead of the 5/8-in.-dia bore of the original valve. The glass flow through this modified freeze valve is not expected to be stopped or even slowed significantly, once flow has been started. But it is expected that the tank can be drained much faster and more completely with the larger bore, and once the tank has drained nearly dry, the valve can again be frozen and reused.

By the end of the report period the CFCM had been reassembled and the melter tank charged with 418 kg of a dry chemical blend of Frit 411 and a simulated SRP waste slurry calcine--this in preparation for a 10-d, continuous glass production test of the modified melter system.

CERAMIC MELTER DEVELOPMENT - J. L. Buelte and S. M. Barnes

As part of the ongoing developmental activities with Savannah River Laboratories, a five-day powdered feed run with simulated Savannah River waste has been completed in the LFCM. Synthetic calcine, simulated with dry chemicals, was premixed with non-premelted glass formers and fed to the melter. This represented a well mixed case and produced no detectable slag accumulation. Even though the melting rate was limited to 51 kg/h due to a foaming condition, rates in excess of 92 kg/h were attained using premelted frit of the same glass former composition. Improved behavior was attributed to the reduced volume of glass released upon melting.

Another major milestone recently completed was the vitrification of 10,000 L of simulated liquid waste in the LFCM. Continuous operation of more than 21 h was completed while liquid-feeding. The process has demonstrated the following:

- elimination of calcination equipment is possible,
- liquid feeding allows excellent mixing of glass formers and calcine,
- physical entrainment of aerosol in the off-gas system is low and remote cold cap level detection is simplified.

Currently, work on liquid-feeding processes is being directed to an expansion of waste types.

The bench-scale ceramic melter (BSCM) was started and brought to operating temperature in November 1978. The bench-scale unit is designed for electrode temperatures in excess of 1400°C. The BSCM has produced 300 kg of defense glass since startup. The first 100 kg was a low-temperature Hanford average composition (with radionuclide removal) meeting the requirements of DOE Milestone 0502-1. In March 1979, 200 kg of a high-temperature glass composition were produced in the melter. During this run the maximum glass temperature noted was 1325°C and feed rates to 14 kg/h were demonstrated. The melter production rate was impaired by feed system limitations, and higher production rates are expected.

This melter has also demonstrated an airlift glass-draining technique. The airlift consists of a 0.25-in.-dia platinum alloy tube inserted into the riser refractory cavity. When air is injected into the riser, as depicted by Figure 15, glass flow is initiated. The airlift drain demonstrated flows in excess of 120 kg/h during the high-temperature run. This method of draining also allowed completion of the high-temperature run after a failure of the front face heater connections. The airlift started and stopped the glass flow rapidly enough that significant glass string and nesting problems did not occur. This draining method has several advantages:

- elimination of flexible connections and the tilting mechanism required by the tilt-to-interrupt-pour drain method
- draining of ~90% of glass present in the melter without a bottom drain
- more immediate glass flow control
- the possibility of being able to drain crystalline or slag material more effectively than current draining methods allow.

FIGURE 15. BSCM Airlift Detail

IN-CAN MELTING DEVELOPMENT - H. T. Blair, P. S. Gorton and H. L. Nielson

Two milestones in the ICM program with DOE were met during this past quarter, as were two milestones in the program with Savannah River Laboratories.

The first DOE milestone was met when a draft of a document summarizing the past four years of ICM process and equipment development at PNL was issued for review and clearance. The document, entitled In-Can Melting Process and Equipment Development from 1974 to 1978, summarizes 54 pilot- and full-scale ICM tests conducted in the nonradioactive demonstration equipment and follows the evolution of the equipment and processing methods to their present states of development.

The second DOE milestone was met by the successful demonstration of the intrinsic-gamma melt-level detection system during the production of two cans of vitrified high-level nuclear waste using the spray calcination/ICM process by the NWVP. Operation of the level detection system was not part of the NWVP, but was performed under the ICM task by personnel from the Physical Sciences Department in conjunction with the NWVP. The equipment clearly indicated when the melt surface passed the level being monitored. These results demonstrate that, provided with a sufficient number of collimators, the gamma-emission melt-level detector will permit the location of the melt surface with a precision of 1 in. during the filling of cans by the ICM process. The detector was also very useful in evaluating the conditions in the

spray calciner following the runs, in characterizing materials in a plugged mist eliminator, and in evaluating the homogeneity of the vitrified product in the filled cans.

The first Savannah River Laboratory commitment was satisfied with the completion of the five-day continual operation of the full-scale spray calciner and ICM using a simulated waste composition and a frit composition defined by Savannah River Laboratory. Four cans 7 ft tall by 2 ft in diameter were filled with a total of 4415 kg of solidified, simulated waste. The objectives of the ICM phase of the demonstration were: 1) to determine the maximum melting rate and minimum complete-fill-cycle time that could be achieved; 2) to evaluate the melting behavior and product of a new sludge composition designated TDS and a new frit composition, 211; 3) to compare the melting rates obtained when only half of the 16 heat transfer plates are used in a 24-in.-dia can; 4) to obtain further data on power consumption and temperature; and 5) to demonstrate the remote connecting section that included a rotating seal.

A melting rate of 85 kg/h was sustained for 6-1/2 h during the filling of a can containing a 16-plate heat transfer assembly. Centerline temperatures in the can during this charging indicated that a higher melting rate would have been possible, but higher calcine generation rates were not possible. The charging rate had to be reduced to 50 kg/h as the melt surface approached the top of the plates. The average melting rate determined by dividing the total batch charged by the total melting time, including 3-1/3 h of heating after charging was terminated, was 59 kg/h. The time to completely process this can, which was approximately 6 ft of melt, was 26-1/3 hours.

The last can processed during the five-day run contained 8 fins instead of 16. The melt centerline temperatures indicate that the batch charging rate of 80 kg/h that was sustained for over 8 h during the filling of the lower portion of the can was at the limit of the melting capacity of the 8-finned, 24-in.-dia ICM. A charging rate of 45 kg/h became too great as the melt surface approached the top of the fins.

The batch (28 wt% TDS waste calcine and 72 wt% 211 frit) did not foam as it melted, and melting appeared to proceed at a relatively rapid rate. However, batch separation did occur at the top of the fins, so that an accumulation of calcine-rich clinkers that would not melt formed in the top of each can.

Between 80 and 87 kW were used by the ICM furnace during the melting of batch at rates of 75 to 85 kg/h, while 52 to 54 kW were required to maintain a filled can at 1070°C. It was also possible to observe the power requirements of a zone increase as the melt rose through it and of a decrease as the melt level rose into zones above.

The second commitment to Savannah River Laboratory was satisfied by using the remote connecting section designed at PNL to link the spray calciner and ICM during the five-day run and by demonstrating a weighing system that successfully monitored the ICM filling. The use of the connecting section demonstrated the ability to make and break connections between the batch delivery tube and the can in the ICM furnace remotely and cleanly. The ability to accommodate thermal expansion and can misalignment without affecting the weighing system while still maintaining a tight seal between the connector and the can was also demonstrated.

EFFLUENT CONTROL - M. S. Hanson

The laboratory-scale spray calciner (LSSC), designed for effluent analysis, completed six operations in this period. A variety of waste feeds were calcined, including SRP and supercalcine.

Decontamination factors were determined for a spray calciner and an off-gas cleanup system consisting of a tube and shell condenser and a venturi scrubber. The decontamination factors are shown in Table 12 for ruthenium and strontium. The strontium is used as a measure of nonvolatile particulate losses.

The factors for the venturi scrubber are greater than those shown, since elemental concentrations were below analytical sensitivity levels.

The gas chromatograph system for measuring permanent gases in process off-gas system gasses was operated during a number of calciner operations and calibrated.

TABLE 12. Spray Calciner Process Off-Gas System Decontamination Factors

<u>Contaminant</u>	<u>Decontamination Factors</u>		
	<u>Spray Calciner</u>	<u>Condenser</u>	<u>Venturi Scrubber</u>
Ruthenium	700	4	>36
Strontium	2400	3	> 3

SPRAY CALCINATION OF SAVANNAH RIVER PROJECT LIQUID WASTE - F. A. Miller

Spray calcination of the Savannah River liquid waste identified in Table 13 has been demonstrated at greater than 400 L/h. This high capacity was achieved by increasing the spray calciner furnace output from 320 kW to 600 kW and by using a higher-capacity liquid atomizing nozzle. A comparison of the new high-capacity nozzle to the previous nozzle is made in Table 14.

TABLE 13. Savannah River Liquid Waste Composition
Based on 1000 Liters Feed Slurry

<u>Constituent</u>	<u>Weight, kg</u>
Fe(OH) ₃	48.8
Al(OH) ₃	12.2
MnO ₂	9.74
CaCO ₃	4.44
Ni(OH) ₂	5.27
NaNO ₃	2.05
Na ₂ SO ₄	1.01
Zeolite	7.24

Other recent equipment improvements include:

1. Supporting the calciner barrel vibrators indepently of the furnace, thus reducing the vibration transmitted to the furnace brick and heating elements and increasing the working life of the furnace.

TABLE 14. Nozzle Comparisons

Characteristics	Previous Nozzle	New High-Capacity Nozzle
Air cap orifice size, in.	0.312	0.547
Approximate maximum liquid flow rate @ 25 psig for good atomization, L/h	320	400
Approximate air flow @ 300 L/h liquid flow, SCFM	30	80

2. Enlargement of the calciner cone discharge flange from 4 in. to 6 in. to reduce the possibility of plugging during high-capacity testing.
3. Providing the option for automatic control of liquid feed flow rate by either varying the atomizing air-flow rate or by varying the feed recirculation line pressure. These two methods of feed rate control are illustrated in Figure 16.

Spray Calciner Tests

Four short-term tests and one five-day test were completed in the first quarter of 1979. During the five-day test the spray calciner was coupled with the in-can melter. This test demonstrated that the full-scale calciner/in-can melter is a variable system for high-capacity immobilization of Savannah River Laboratory radioactive wastes in glass. Glass production rates of greater than 80 kg/h were achieved. Table 15 summarizes the tests made this quarter. Figure 17 illustrates that a graph of spray calciner power consumption versus liquid flow rate, using data from the five-day test, is approximately linear over the flow range tested.

FIGURE 16. Two Methods of Liquid Feedrate Control

TABLE 15. Spray Calciner/In-Can Melter Tests

Test Parameters and Units	Spray Calciner Test Numbers				
	23	24	25	26	27
Run time, h	6-1/2	5	77	3	2
Maximum liquid feed flow rate, L/h	360	325	338	300	420

FIGURE 17. Spray Calciner Power Consumption

REMOTE LAB-SCALE VITRIFICATION PROGRAM - C. A. Knox

The equipment design for the remote lab-scale vitrification program to be operated in D-Cell of the 324 Building was completed and bids were let. The system was divided into three packages for bid-letting: a feed system, a spray calciner, and an off-gas system. Each package is being fabricated by an off-site vendor as a single modular unit. The three modules will be piped together after they are installed in the cell. Design was also completed on a core and plug to be installed in the south wall of D-Cell to accommodate the service piping for the remote lab-scale vitrification system. Design was begun on the electrical and instrumentation installations and on the support jumpers for this system. A quality assurance plan for this program was drafted and approved, and a design document describing the remote lab-scale vitrification system was written.

REFERENCES

- Blair, H. T. 1976. Vitrification of Nuclear Waste Calcines by In-Can Melting. BNWL-2061, Pacific Northwest Laboratory, Richland, Washington.
- Bonner, W. F., et al. 1976. Spray Solidification of Nuclear Waste. BNWL-2059, Pacific Northwest Laboratory, Richland, Washington.
- De, A. K., et al. 1976. "Development of Glass Ceramics for the Incorporation of Fission Products." Bull. American Ceramic Society, 55(5), 500-503.
- McElroy, J. L. 1975. Quarterly Progress Report, Research and Development Activities, Waste Fixation Program: April to June, 1975. BNWL-1932, Pacific Northwest Laboratory, Richland, Washington, p. 20-21.
- McElroy, J. L. et al. 1979. Quarterly Progress Reports - Research and Development Activities - High-Level Waste Immobilization Program: January through December, 1978. PNL-2999-4, Pacific Northwest Laboratory, Richland, Washington.
- Ringwood, A. E. et al. 1979. "Immobilization of High-Level Nuclear Reactor Wastes in SYNROC," Nature, 278, p. 219.
- Simonen, F. A., J. A. Griffiths and M. J. Thurgood. 1978. "Analysis of a Canister Closure Design by Damage Tolerance Concepts," ASME 78-PUP-108, Presented at Joint ASME/CSME Pressure Vessels and Piping Conference, June 1978, Montreal, Canada.
- Simonen, F. A., and S. C. Slate. 1979. Stress Analysis of High-Level Waste Canisters: Methods, Applications, and Design Data. PNL-3036, Pacific Northwest Laboratory, Richland, Washington.
- Volf, M. B. 1961. Technical Glasses. Sir Isaac Pitman and Sons, LTD, London.

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