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Quarterly Progress Reports Research and Development Activities – High-Level Waste Immobilization Program: January Through December 1978

J. L. McElroy W. F. Bonner
J. E. Mendel M. H. Henry

May 1979

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

Pacific Northwest Laboratory
Operated for the U.S. Department of Energy
by Battelle Memorial Institute

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DISCLAIMER

FOREWORD

This volume contains the four quarterly reports of the High-Level Waste Immobilization Program for 1978. The accomplishments of each quarter are described separately, and each quarterly report has been assigned its own PNL number. The 1978 HLWIP Quarterlies have been bound together only to expedite their release. In the future our quarterly reports will again be issued as individual documents.

PNL-2999-1

HLWIP QUARTERLY REPORT
JANUARY THROUGH MARCH 1978

PNL-2999-1
UC-70

QUARTERLY PROGRESS REPORT
RESEARCH AND DEVELOPMENT ACTIVITIES
HIGH-LEVEL WASTE IMMOBILIZATION PROGRAM: JANUARY THROUGH MARCH 1978

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Pacific Northwest Laboratory
Richland, Washington 99352

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 1978:

- Approximately 9000 kg of defense waste glass were processed through the liquid-fed ceramic melter and drained into six canisters 2 ft in dia by 9.5 ft tall, using either standard tilt-pour operation or a newly developed air-lift draining technique.
- A crystalline sludge layer of $NiFe_2O_4$ spinel (with Mn and Ti in solid solution) has accumulated on the bottom of the ceramic melter. Efforts to flush out the sludge during normal operation were unsuccessful.
- Microstructural examination of devitrified specimens of four different fully radioactive glasses revealed minor differences in crystalline species from those occurring in nonradioactive counterparts of the glasses. The uranium concentrations in the radioactive glasses were found to be 2 to 3 times those planned, and that is believed to account for all of the differences.
- Corrosion coupons taken from the laboratory spray calciner after operation with fluoride-containing simulated Thorex waste showed acceptable corrosion rates of 0.2 mil/mo or less for 300-series stainless steels, and 0.6 mil/mo or less for Inconels.
- Cesium volatility from supercalcine was found to be about 25 times lower than it was from waste glass.

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 and -2265-4.

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JANUARY THROUGH MARCH 1978

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 FIXATION PROCESS DEVELOPMENT

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

JOULE-HEATED CERAMIC MELTER - C. C. Chapman and J. L. Buelt

During the last quarter, progress toward completion of the calcine-fed ceramic melter coupled to the full-scale spray calciner has proceeded on schedule. The differences in waste glasses that are being processed in large-scale engineering equipment have indicated that melting and glass chemistry should receive greater emphasis. Problems with reboil, foaming at the reaction interface, and sludge formation in process equipment of newly proposed glasses for the various existing radioactive wastes and anticipated wastes have indicated that certain screening tests need to be completed for newly proposed waste glass compositions before they are committed to large-scale tests. A new activity area, "Process Chemistry" has become an important part of the process and equipment development program. Newly proposed glasses will be evaluated from a process perspective prior to ordering large quantities of chemicals and initiating long-term experiments. During the period of January through March 1978, the liquid-fed ceramic melter (LFCM) has been tested with various compositions. A total of 9000 kg of glass has been processed, and six canisters 2 feet in dia and 9.5 feet tall have been filled. A set of experiments was completed in which the same final glass composition was produced by adding several different chemical blends to the melter. The results of these short-term experiments are indicative of the meltability of various chemical blends in a continuous melter. Significant variations (as much as a factor of three) were noted between various chemical blends. The use of an air-lift concept to drain glass has been demonstrated to be an effective alternative to tilt-pour operation. Flow rates obtained using airlifting for the given geometry in the LFCM showed that rates as high as 260 kg/hr could be maintained, and a pump-down of one third the depth of the melter was demonstrated.

As a result of closer examination of glasses processed in the last quarter, we have discovered that some of the glass compositions processed have a relatively high liquidious temperature. A simulated Savannah River waste glass yielded 3% to 6% $NiFe_2O_3$ spinel at 1100°C. Because the floor of the LFCM operated below 1000°C, an accumulation of the spinel-sludge or crystals occurred over several months of operation. Out-gassing from the cool, sludge-laden floor has caused problems in the stable operation of the LFCM during processing tests. After a short period of feeding to the system, the operating temperature of the floor begins to increase slowly. This increase in temperature apparently causes a release of gas in the glass. This is attributed to the reduction of gas solubility in the glass, or a gas release when the crystals dissolve back into the glass. If the batch blanket covers the entire surface of the melter, an accumulation of gas bubbles results beneath the blanket. Ultimately, the release of the gas occurs through the blanket. The foaming glass engulfs unreacted material in the blanket and causes further gas release. This yields further foaming and frothing. Attempts to remove this sludge by increasing the floor temperature, agitation by air bubbles, or flushing with frits has improved the condition. The experience with reboil in the LFCM has not been duplicated in the laboratory. However, its procedure of maintaining the floor and the body of the molten glass at the highest possible temperature while not processing has significantly mitigated the out-gassing or reboil during process tests. Further evaluation of this phenomenon is needed. The processing of several significantly different waste glasses in the same melter may be the source of the re-boil problem and needs to be considered in the evaluation and identification of the out-gassing problem.

During a process experiment with a simulated defense waste glass, difficulties with foaming at the fusion layer were encountered. The generation of gas bubbles in the reaction layer dramatically reduced the process rate. The cause of this surface foaming has been attributed to the decomposition of sodium carbonate in the highly viscous glass frit additive. A short follow-up experiment using glass-forming chemicals or a chemical blend resulted in improved process rate without foaming in the reaction zone. To assess the advantages of various chemical blends of minerals and/or glass frits, a series of eight short experiments were developed. The listing of simulated calcine and glass formers is given in Table 1. In each of the eight experiments, over 400 kg of material were fed to the LF ceramic melters using similar operating procedures. The cold cap thickness and subsequent melt-down times after termination of feeding were determined for each of the chemical blends. Total glass production for each of the tests was as follows: SRP-3, 2990 kg; SRP-4, 390 kg; SRP-5, 400 kg; SRP-6, 400 kg; SRP-7, 450 kg; SRP-8, 400 kg; SRP-9, 370 kg; SRP-10, 440 kg.

A typical feed rate schedule and power consumption are given in Figure 1, a cold cap diagram is illustrated in Figure 2, and the resulting cold cap thicknesses and melt-down times are given in Table 2. As can be noted, differences in the cold cap thicknesses at the end of the feeding and the required melt-down time after feed termination vary by a factor of from three to five. These results are indicative of the meltability for the various chemical blends, and demonstrate that a glass composition can be produced from many different chemical blends and that the processability of different blends can vary significantly.

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

A crystalline sludge layer has accumulated on the floor of the ceramic melter. Elemental analysis and x-ray diffraction (XRD) of sludge samples identify a $NiFe_2O_4$ spinel with manganese and titanium in solid solution. This phase is a remnant from the previous Savannah River Plant (SRP) ceramic melter trials (8/77 to 10/77). Laboratory melts of the SRP "average" glass clearly show the formation of the insoluble crystalline phase after 1 hr at 1100°C. The large density difference (5.2 g/cc vs 2.7 g/cc) between crystals and glass accounts for the settling observed after 158 hours.

Although the crystalline phase is insoluble in the SRP "average" glass, approximately 2 vol% will dissolve in 77-268, 76-107, and 76-199 frits after 1 hr at 1100°C. Thixotropic viscosity behavior of crystal/glass melts, crystal settling, and foaming severely limit the removal of sludge during normal melter operation. Melter overflow samples collected during a variety of stirring and pouring operations did not contain any crystalline material.

TABLE 1. Savannah River Ceramic Melter Batch Melting Tests

		Glass Batch, wt%								Final Glass Compositions		
	Constituents	Test SRP-3	Test SRP-4	Test SRP-5	Test SRP-6[(a)]	Test SRP-7[(a)]	Test SRP-8[(b)]	Test SRP-9	Test SRP-10	Tests SRP -3 to -8	Test SRP-9	Test SRP-10
Spray	Na_2CO_3	(c)	32.2	32.2	32.2		32.2	32.2	21.1			
Calciner	$CaCO_3$		3.1	3.1	3.1	4.5	3.1	3.1	3.2			
Feed	$Fe(OH)_3$		21.5	21.5	21.5	31.7	21.5	21.5	24.0			
	$Al(OH)_3$		36.1	36.1	36.1	53.3	36.1	36.1	40.0			
	MnO_2		5.4	5.4	5.4	7.9	5.4	5.4	8.7			
	$Ni(OH)_2$		1.3	1.3	1.3	2.0	1.3	1.3	2.6			
	Na_2SO_4		0.4	0.4	0.4	0.6	0.4	0.4	0.4			
Glass	SiO_2	31.8	48.5	49.9	60.4	52.5	60.4	58.3	60.4	39.4	42.6	40.7
Formers	Na_2O	19.2			6.3	18.5	6.3	7.1	6.3	13.9	15.0	10.1
	B_2O_3				11.5	10.0	11.5	13.0	11.5	7.5	8.1	7.7
	CaO				5.7	4.9	5.7	6.4	5.7	4.6	4.9	4.7
	Li_2O				4.6	4.0	4.6	5.2	4.6	3.0	3.2	3.1
	TiO_2	6.0	9.2	10.5	11.5	10.0	11.5	11.5	11.5	7.6		7.7
	Fe_2O_3	6.8								8.4	9.1	8.5
	Al_2O_3	9.9								12.3	13.3	12.4
	MnO_2	2.3								2.8	3.0	4.1
	NiO	0.5								0.6	0.6	1.0
	Na_2CO_3		8.6	1.7								
	H_3BO_3	10.7	16.4									
	$CaCO_3$	6.7	8.1									
	Li_2CO_3	5.9	9.1									
	$Na_2B_4O_7$			15.3								
	$CaSiO_4$			10.7								
	$LiOH \cdot H_2O$			11.8								
	Na_2SO_4	0.2										

(a) Frit added in premelted form.
(b) Frit added in premelted form, except that TiO_2 was mixed as a separate powder.
(c) Fed as dry chemicals.

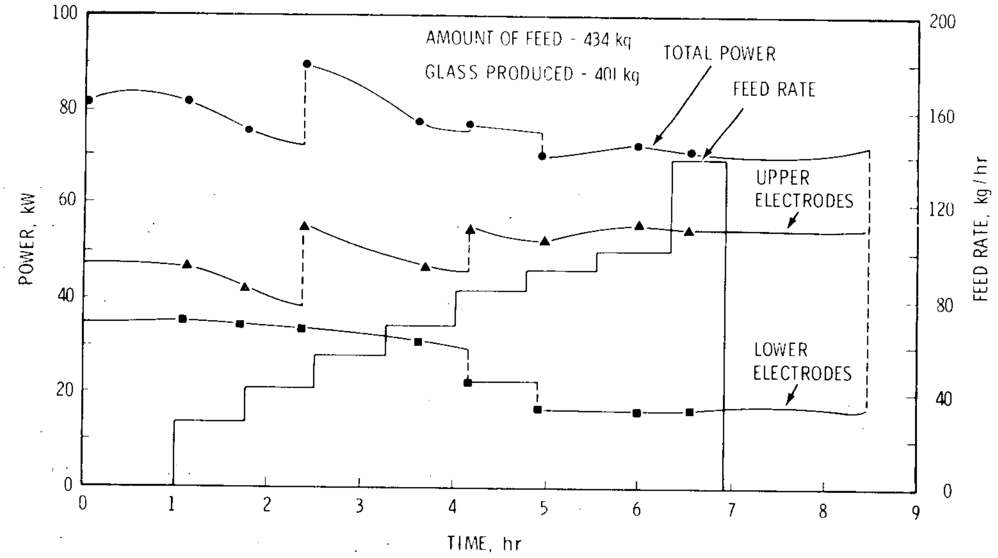

FIGURE 1. Typical Feed Rate Schedule and Power Consumption

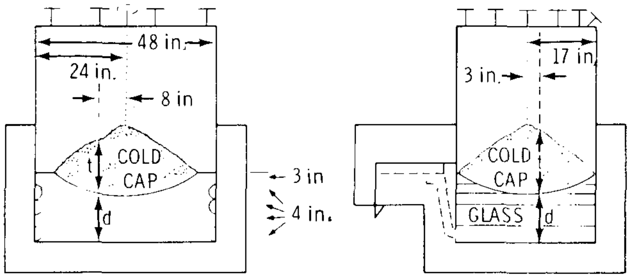

FIGURE 2. Cold Cap Thickness Diagram

TABLE 2. Cold Cap Thicknesses and Melt-Down Time

Run Number	Cold Cap Thickness, in.	Molten Glass Depth, in.	Meltdown Time, hr
SRP-4	16	15.5	3.6
SRP-5	6.5	19.5	1.8
SRP-6	8	18	1.5
SRP-7	9	17	2
SRP-8	12.5	16	(a)
SRP-9	20.5	15.5	5.5
SRP-10	19.5	11.5	10.3

(a) Run SRP-9 followed SRP-8 without a meltdown of the cold cap.

Samples of the SRP "composite" glass batch to be used in future ceramic melter trials were examined for potential problems. Laboratory tests showed this composition to melt more rapidly and foam less than the previous SRP "average" glass batches. The melt viscosity of the as-received material was comparable to values reported by SRP. There was no indication of crystalline precipitation and settling, as had been noted for the "average" composition.

Progress this quarter was marked by completion of five spray calciner runs. The main emphasis of these runs was to establish the ability of the spray calciner to process defense waste feed compositions. Preliminary work to develop compatible feed solutions and process conditions that permit calcination of complete glass compositions has been done.

IN-CAN MELTING - H. T. Blair

The original in-can melter (ICM) concept had the canister suspended in the furnace from bails on the top of the can. The can extended through the top of the furnace to provide access to these bails. This placed the top of the can in a thermal gradient, which resulted in the accumulation of unvitrified calcine inside the can above the melt level. In the PNL full-scale (FS) ICM the can is supported at the bottom and the entire can is inside the furnace chamber.

Loose material was collected from the surface of the product of FS ICM-17 and tested for leach resistance to determine whether or not locating the complete can inside the furnace has eliminated the existence of unvitrified calcine in the can following the ICM process. The material collected is spall from the inside walls of the can and the surfaces of the fins, which extend above the melt surface. Because this spall contains iron oxide from the can material, a magnet was used to separate the sample into magnetic and nonmagnetic fractions to reduce the effects of this variable. The results of the 72-hr Soxhlet leach test are reported in Table 3.

TABLE 3. Soxhlet Leach Test Results for Spall from Inside FS ICM-17

Sample ID	Wt% Lost in 72 hr
FS ICM-17 Bulk Sample	4.1
FS ICM-17 Nonmagnetic	2.4
FS ICM-17 Magnetic	5.7

These results indicate that the spall present in the top of cans filled in the FS ICM has leach resistance of the same magnitude as that of the bulk of the vitrified product in the can.

During the ten-day continuous demonstration of the ICM process last year, we became aware of the need to develop and demonstrate a satisfactory method of remotely positioning the canister in the furnace and making and breaking the connection between the canister and the calciner when exchanging empty canisters with full ones. The responsibility for identifying a concept and designing and building a demonstration unit for incorporation into the full-scale spray calciner/ICM was accepted by Philip S. Gorton of the Engineering Physics Department. Phil has defined the following design criteria for the remote connecting section and canister support system:

1. The remote connecting section's function is to convey a calcine and frit mixture from the diverter into the can and to convey a counter flow of off gas from the ICM to the diverter. The function of the ICM can-support system is to position and support the can in the furnace and to monitor the weight and rate of weight change of the can contents during the ICM process.
2. The operations that are to be performed by this equipment are as follows:[a]
   - lower empty can into open ICM furnace and center on the bottom support
   - disengage handling bail from can
   - place insulating cap on furnace
   - rotate connecting section into position over furnace
   - lower fill spout into mouth of can
   - apply sealing force between can and spout without compromising load cell function
   - open cone valve at end of spout

---

[a] These operations are not necessarily listed in the order in which they must be performed, and operations may be combined.

- proceed with ICM process including heatup, diverting batch into can, filling with melt, diverting batch away from can, and cooling
- close cone valve
- release sealing force between can and spout
- retract spout from mouth of can
- rotate connecting section away from top of furnace
- remove insulating cap from furnace
- engage handling bail in mouth of can
- remove can from furnace.

3. All of the operations listed in Item 2 are to be accomplished remotely without the aid of master-slave manipulators. An overhead crane and an air wrench suspended from the crane are available for routine operations.
4. The can to be used is a right-circular cylinder with a flat or concave bottom and a flat top, having approximately a 5-in.-dia opening in the center. The present design has a three-lug twist lock around the opening.
5. A metallic E-ring seal will be used in the mouth of the can, and it will require a sealing force of 25 ft-lb/cir.-in. to be applied to it in order to effect a seal between the can and the spout.
6. The can is to be supported from the bottom in the furnace by being set on a refractory material plug; the plug rests on load cells so that the weight of the can's contents may be monitored.
7. The connecting section must have a flexible joint in it, such as a bellows or telescoping sleeve, to allow the can to rest unrestrained on the load cells.
8. The furnace is to be fixed in position in the cell so that all service leads to it and the load cell system can be made stationary.
9. The connecting section that will join the outlet from the diverter to the mouth of the can must rotate to one side of the furnace when disengaged from the can's mouth to permit cans to be exchanged through the top of the furnace.
10. The entire can will be placed within the furnace so that the top of the can will be between four and six inches below the top of the heated chamber of the furnace.
11. The spout at the end of the connecting section which engages in the mouth of the can must pass through the insulated cap on the furnace and is subjected to an extreme thermal gradient, ranging between 300°C and 1050°C. The spout must be water-cooled to prevent batch from melting on its lower end.
12. The spout must be sealed closed whenever it is not engaged into the mouth of a can.
13. A disperser (presently cone-shaped) must be available in the spout so that it can be lowered through the mouth of the can during batch charging to deflect batch away from the center of the can. This disperser must also be water-cooled to prevent batch from melting on it.

14. The devices used to perform these operations should be made as simple as possible to reduce failure potential and service requirements.

15. All materials of construction including seals, lubricants, and electrical insulation must be able to withstand gamma radiation levels of 10^6 rad/hr and neutron levels of 200 rad/hr.

16. All materials of construction must be able to withstand nitric acid-contaminated air environments, high humidity, and sustained temperatures as high as 120°C.

Control of the ICM process requires a knowledge of where the melt level is at all times during the filling of the canister. We also desire to know when unmelted batch is accumulating in the can and where it is being deposited. Further, it is desirable that this information be determined using monitoring devices outside of the melter. One promising method of monitoring the filling of the ICM is to scan the gamma radiation from the waste in the canister. Dr. Ronald L. Brodzinski of the Physical Sciences Department has demonstrated that by doing this we can discriminate between melted and unmelted batch and locate a melt surface to ± 1/2 inch. We are now preparing to demonstrate this technique during the actual ICM processing of two canisters of vitrified waste for the Nuclear Waste Vitrification Project.

Six holes will be drilled from the outside in the walls of the process cell for the placement of collimators to be used with the gamma detector. The holes will not penetrate the stainless steel liner of the cell, nor the last 2 in. of concrete in the wall. The diameters of the holes will be 1-1/2 in. for 3 ft into the wall and 3/4 in. for the remaining distance. Four of the holes will be located in the west basement wall to provide access to the ICM. The other two holes will be located in the first floor north wall so that the filter housing and cone under the calciner can be monitored. The collimators will be made by casting lead in 3-ft lengths of 1-1/2-in.-dia schedule 40 pipe.

All presently used frits are manufactured by a water quenching process. Unfortunately, this depletes the surface layers of the frit of alkali (mainly sodium) and generates numerous microcracks in the surface, which allow a rather high water adsorption. Such water cannot easily be driven off, even at elevated temperatures. As a result, such frit tends to foam upon remelting and thus slows the melting process, both by the lack of sodium and by the presence of the thermally insulating foam layers. It has been common industrial practice in such situations to add extra alkaline to the melt, thus compensating for the sodium loss during the water quenching. A frit with an extra-high sodium content would presumably compensate for sodium depletion, even though foaming would not be affected.

FLUIDIZED-BED CALCINATION - J. C. Hartl

Two runs have been made with the modified fluidized-bed calciner (FBC) during this reporting period. This FBC is shown in Figure 3. The first run (FBC-II-1) was a shakedown run using an acid-type waste. The results of FBC-II-1 indicated a higher than expected fracturing rate in bed material. The next run (FBC-II-2) was done with simulated Redox waste. A larger-sized bed material was used, and appears to have compensated for bed material fracturing.

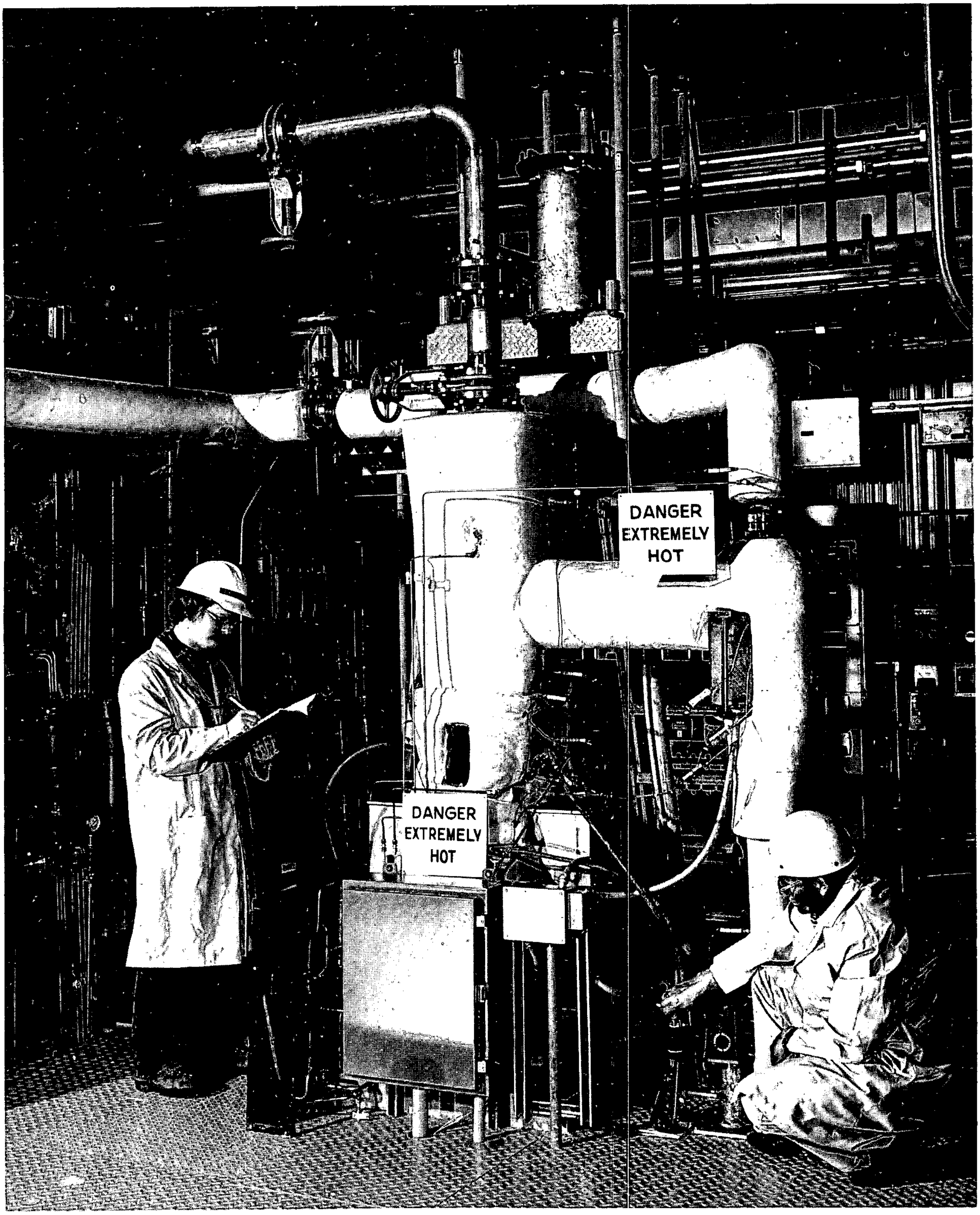

FIGURE 3. Modified Fluidized-Bed Calciner

EFFLUENT STUDIES - M. S. Hanson

The laboratory spray calciner was operated this quarter with a fluoride-containing simulated Thorex waste. The operation produced dry, easily vitrified calcine. Off-gas sampling, condensate monitoring, and corrosion coupons placed strategically throughout the system all indicated that fluoride volatility was sufficiently low to prevent unacceptably high corrosion rates. Stainless steels of the 300 series showed corrosion rates of 0.2 mils/mo or less, while the Inconel metals had 0.6 mil/mo rates. Microscopic examination of 316 SS sintered metal filter samples showed no significant corrosion.

A candidate material for the adsorption of volatilized ruthenium from calciner off gas has been defined and produced. The material is a glass frit (76-199) coated with Fe_2O_3 and fired, producing a 4-wt% iron oxide adsorbent. The adsorbent is being tested in the off-gas train of the laboratory-scale spray calciner during a long-term (50-hr) run at this time.

A pilot-scale spray calcination run was made with simulated PW-9 feed containing 50% of the nominal ruthenium concentration. Ruthenium and tellurium losses were 0.044% and 0.039%, respectively. There was no detectable loss of cesium from the calciner.

SECTION 2 - WASTE FORM CHARACTERIZATION

The purpose of waste form characterization is to measure the properties of candidate solidified products and containers (solidified waste and canister) as functions of composition, processing parameters, and storage conditions. The measurements are used to: 1) ensure operability of the vitrification processes and 2) provide data for safety analyses of high-level waste management. The ultimate goal of waste characterization 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 a final disposal site, we may be fully confident that their behavior is understood and that any changes or interactions with their environments are wholly predictable.

THERMAL EFFECTS UPON STORED GLASS - J. H. Westsik, Jr.

Density and total open porosity of specimens of 77-260[PW-7c-3(1:2)77-269] and 77-107 [PW-9-3(1:2)77-268] glasses were measured after storage for 2 mo at 300°, 400°, 500°, 600°, 700°, 800° and 900°C. Neither glass showed significant variation in density or porosity as a result of the long storage period at elevated temperatures. Porosity was always less than 1%. The average density of both glasses is 3.06 g/cm^3.

Glass leach rates of 76-68 [PW-8a-3(1:2)76-101] based on cesium and strontium are plotted in Figures 4 and 5. The curves in each figure represent the leach rates of the as-melted glass and of the sample with the highest crystallinity, obtained by holding the sample for 2 mo at 750°C. After an initial rapid decrease in the leach rate, the glass leachability is remaining relatively constant. The increased crystallinity causes a small increase in the leach rate of the glass. Leach rates based on uranium of the as-melted glass are shown in Figure 6. The leach rates are a factor of three lower than those calculated from cesium or strontium.

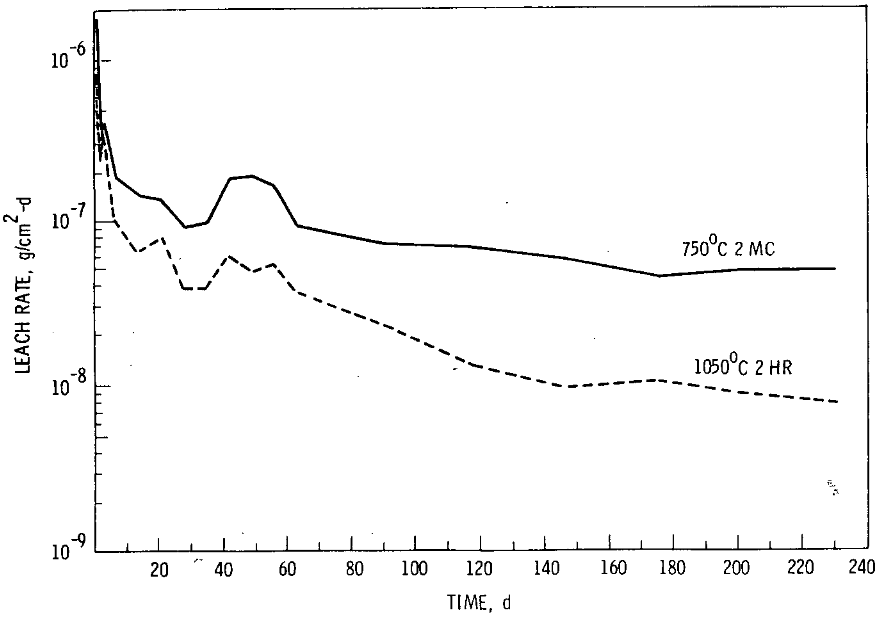

FIGURE 4. Long-Term Leach Rates of 76-68 Glass Based on Cesium

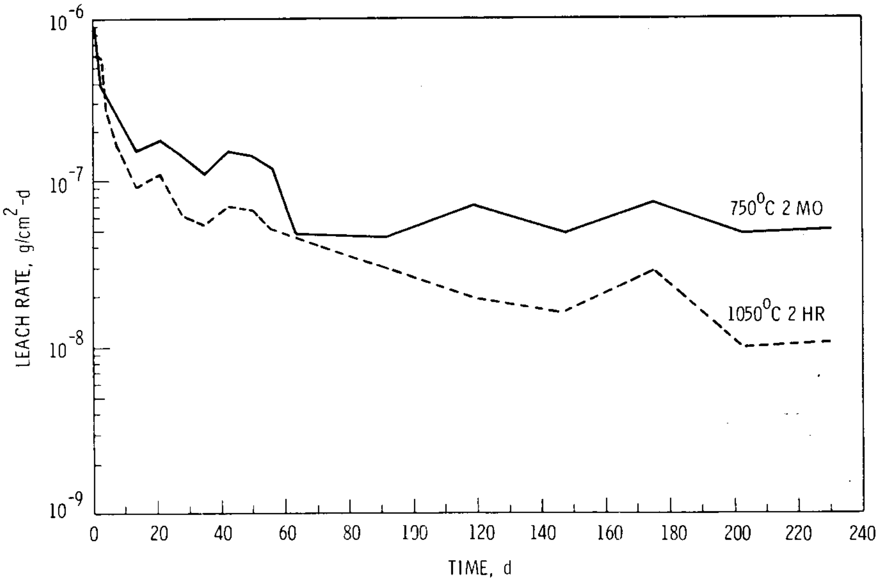

FIGURE 5. Long-Term Leach Rates of 76-68 Glass Based on Strontium

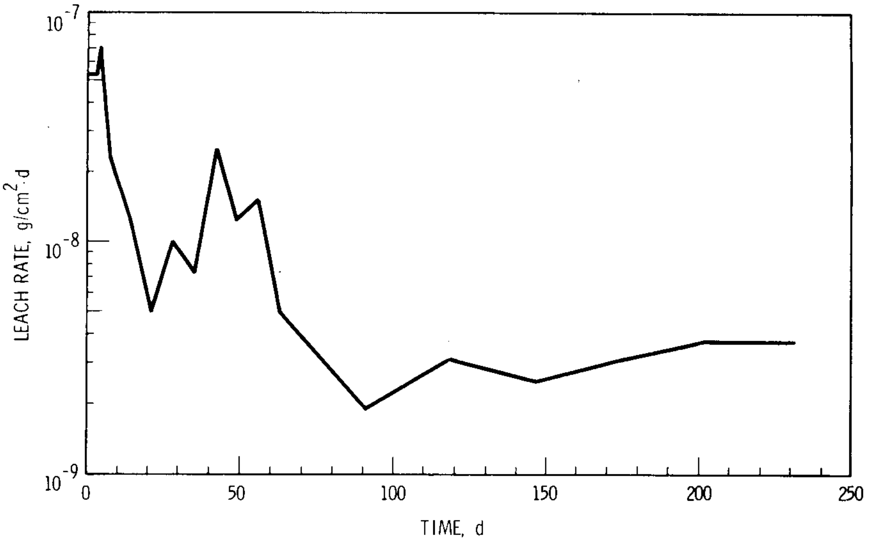

FIGURE 6. Leach Rate Based Upon Uranium of 76-68 [PW-8a-3 (1:2) 76-101] Glass

PHASE BEHAVIOR - J. W. Wald

This quarter we conducted analyses on two additional glass waste compositions, bringing the total under examination to four. These glasses are described in Table 4. Measurements of relative percent crystallinity based on integrated areas of the x-ray diffraction (XRD) traces for samples slow-cooled (∿6°C/hr) from the melt temperature were: 76-68 = 8%, 77-260 = 27%, 77-107 = 35%, and 72-68 = 43%. The major phase observed in 77-260 glass was found to be a rare earth titanate, while in 77-107 glass the major phase was a MO_2 phase of the fluorite structure type.

Studies on four fully radioactive glass compositions similar to the ones above (except for higher than normal uranium concentration) indicated the presence of some phases not seen in the simulated products processed under the same time/temperature conditions. The

TABLE 4. Principal Characteristics of Glasses Undergoing Comparative Microstructural Examination

Glass	Characteristics
72-68	High Zn glass frit; clean waste stream
76-68	High Fe + Na waste stream
77-107	Clean waste stream
77-260	High Ti + Cu glass frit; high Gd + Na waste stream

uranium content (2 to 3 times expected concentrations) causes additional uranium-containing phases to form; though not fully characterized as yet, they have been found by microprobe analysis to contain Zn, Ca, and Si as primary constituents. Although the full-level radioactive glasses were not identical in composition to their nonradioactive counterparts, the microstructure of both vitreous and devitrified samples were equivalent to or better than the nonradioactive glasses.

Continued quantitative studies on the 76-68 glass still show that this glass is quite stable thermally, with low concentrations of devitrification products. Comparisons of simulated and full-level radioactive 76-68 glass with four times the expected uranium content suggest a desirable insensitivity to broad compositional differences with little effect upon overall quality. This was the only glass prepared that was insensitive to the high uranium loading.

THERMAL AND MECHANICAL SHOCK - L. R. Bunnell

Samples of glass composition 77-260 were prepared in both the vitreous state (poured into graphite mold at 1100°C and furance-cooled from 500°C) and after devitrification (cooled from 1100°C at 6°C/hr). Examination by metallography confirmed that the devitrified specimen contained substantially more crystalline phases, principally RuO_2, metallic Pd, and $Gd_2Ti_2O_7$. X-ray diffraction showed the percentage of crystalline phases to be $\sim$27%, as compared with 3% in the vitreous state.

Standard (1.1 cm in dia x 1.3 cm high) cores were drilled from the two glass types, and were impact tested at 160 ft-lb (217 joules). The sieving results are plotted in Figure 7; there is no difference between the particle sizes produced in the two conditions, at least above 37 μm.

Impact experiments performed on this glass and on other compositions subjected to a simple slow-cool devitrification appear to show no benefits from a toughness point of view; the slow-cool is also equivalent to the cycle likely in the case of actual heat-producing waste.

In an attempt to provide a simple test for characterizing waste glass strength that is easily adaptable to hot-cell work, the Brazilian (or diametral) compression test was tried. Since the previous data base was small and the scatter high, the test was used on a larger number of soda-lime-silica and ICM-11 glass samples. Samples were prepared by diamond-drilling and diamond-sawing, with no further preparation, and were handled identically. Results are tabulated in Table 5.

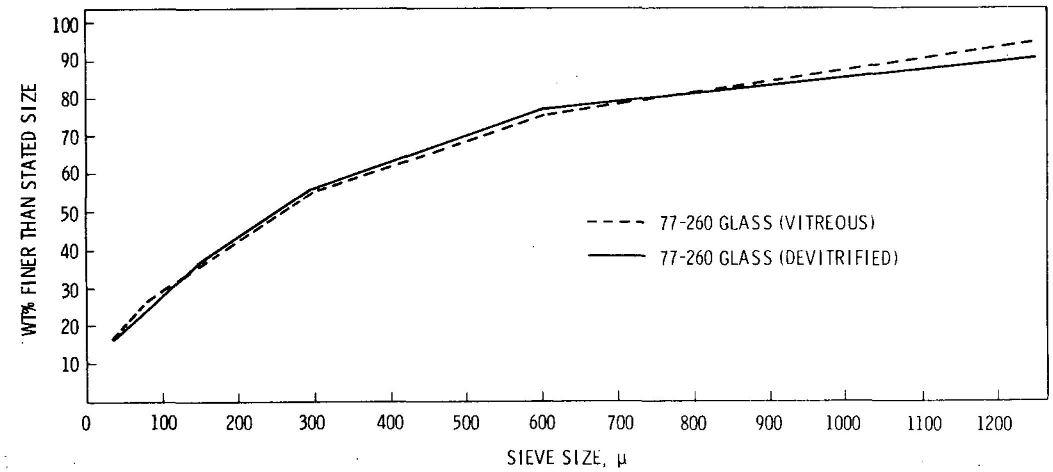

FIGURE 7. Sieve Size Analysis for Vitreous and Devitrified 77-260 Glass Tested at an Impact Energy of 160 ft-lb

TABLE 5. *Tensile Strength of ICM-11 and Soda-Lime-Silica Glass*

Glass Type	Number of Samples Tested	Average Strength, psi	Standard Deviation, psi
ICM-11	29	5393	1017
Soda-Lime-Silica	32	6913	1820

Variability is still higher than desired, but the above results probably are about what can be expected in practice. A fairly large number of specimens will be required for work of this type, and changes in the glass (i.e., as a result of radiation damage) will have to be quite large to be statistically significant.

VAPORIZATION STUDIES - W. J. Gray

Vaporization results for the waste glass 72-68 have been published (Gray, 1976) together with a description of the apparatus, experimental procedures, and treatment of data. As a continuation of this study, the effect of additives on the volatility of cesium and other elements is being investigated.

Figure 8 shows weight loss results at 1100°C for 72-68 glass containing Al_2O_3 additions in the range of 0 to 15 wt%. Weight loss rates were reduced by a factor of about 2.7 with the addition of 15% Al_2O_3. If it is assumed that the compounds $MAlSiO_4$ and $MAlSi_2O_6$ (where M represents an alkali element) are formed, then about 10.7 wt% Al_2O_3 is required to accommodate all the alkali elements in 72-68 glass.

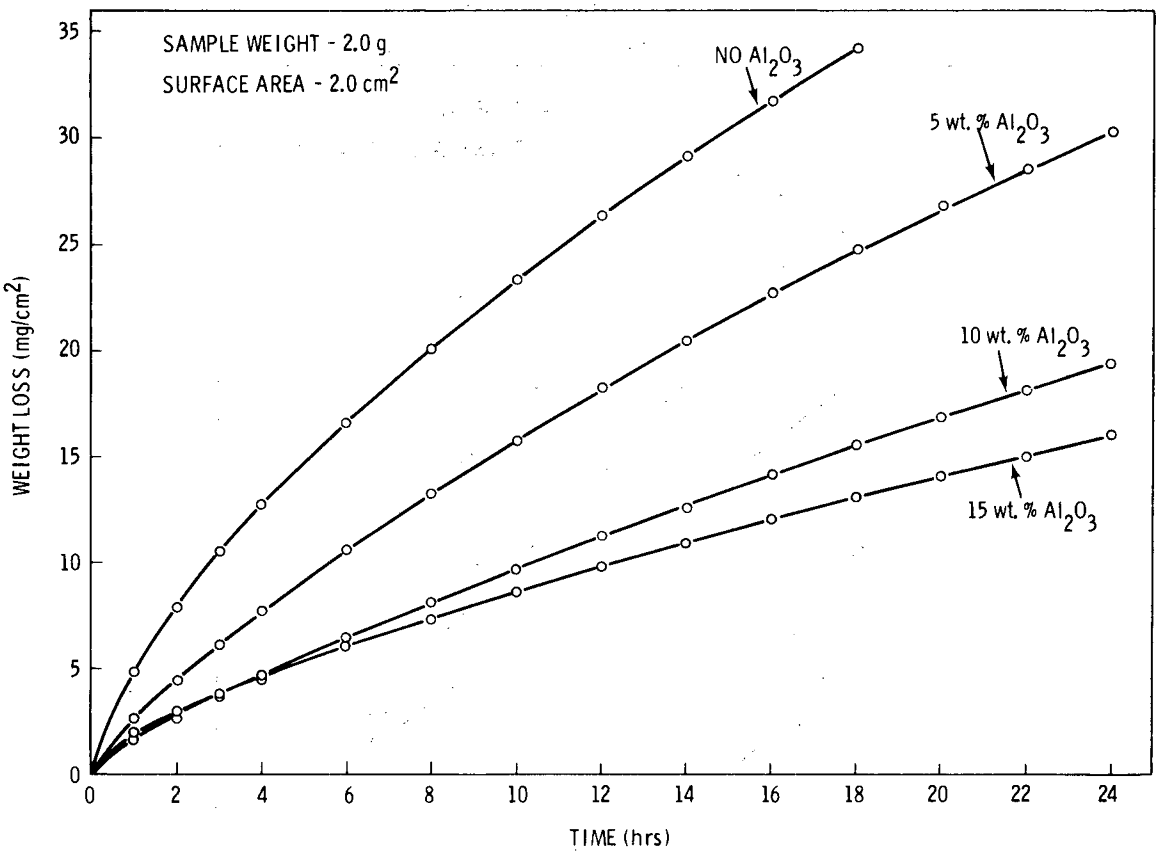

FIGURE 8. Weight Loss in Dry Air at 1100°C for 72-68 Glass Containing Various Amounts of Al_2O_3

Figures 9 and 10 show the effect of 10% Al_2O_3 on the weight loss of individual elements. Use of conservative data treatment methods is reflected in Figure 8 by the indication of 100% loss of Cs from 72-68 glass after 4 hr at 1200°C. It is known that less than 100% of the Cs is vaporized under these conditions. Aluminum oxide had little effect upon B, Na, and Ru losses, while the loss of each of the other elements was reduced by factors of 2 to 3. These results suggest mechanisms other than the formation of alkali alumino silicates must be responsible for the reduced weight loss rates.

Figure 11 shows gross weight loss results at 1100°C for 76-183 glass with various amounts of TiO_2 substituted for SiO_2. Table 6 shows the effect on individual elements. Again, the effect on B, Na and Ru was smaller than for the other elements.

The effect of Al_2O_3 and TiO_2 on volatility was in opposite directions, but was rather modest in both cases. The effect on elements of dissimilar chemistry was remarkably uniform, while at the same time sodium was affected in a different way than were the other alkali elements. All this seems to suggest a mechanical rather than chemical effect upon volatility. There is possibly a correlation with viscosity. The effect of TiO_2 on viscosity is not as well established, although it is thought to <u>reduce</u> it somewhat.

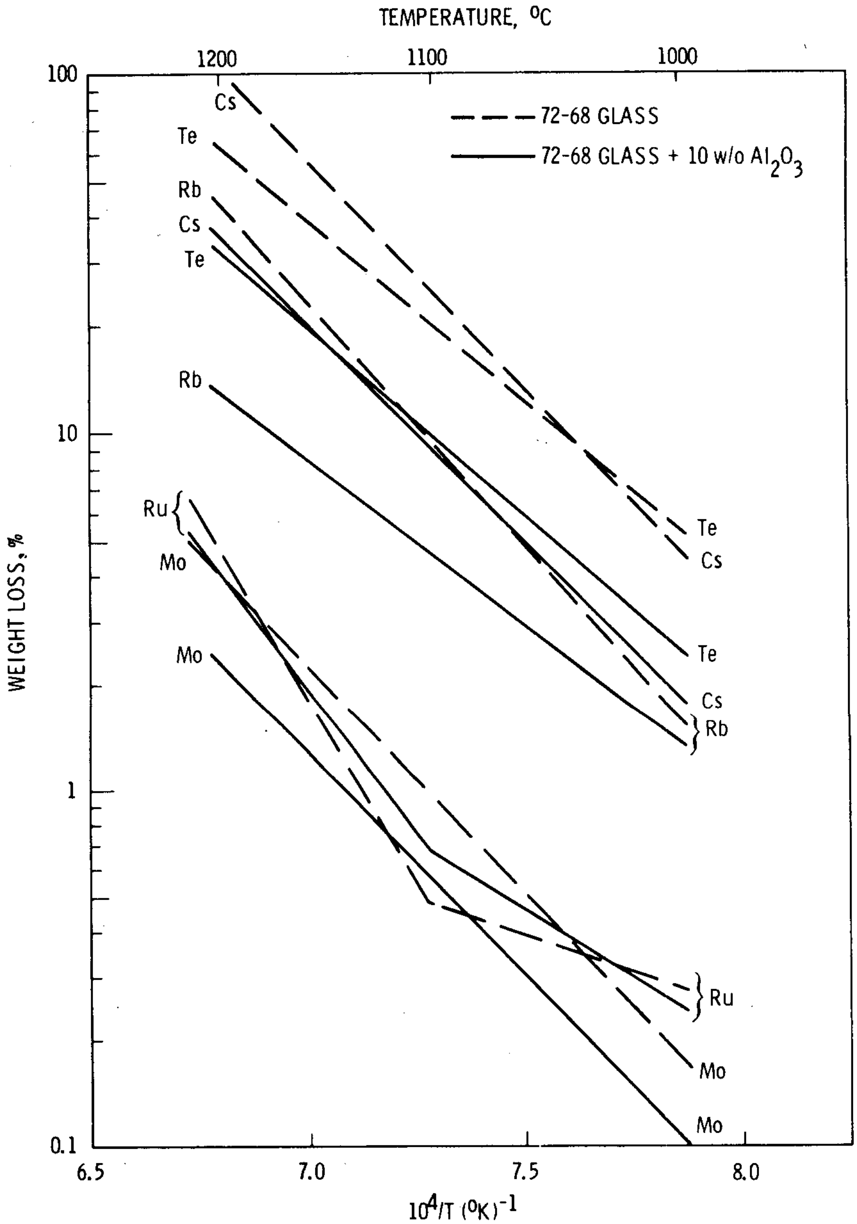

FIGURE 9. Fractional Weight Loss of Individual Elements After 4 Hr in Dry Air

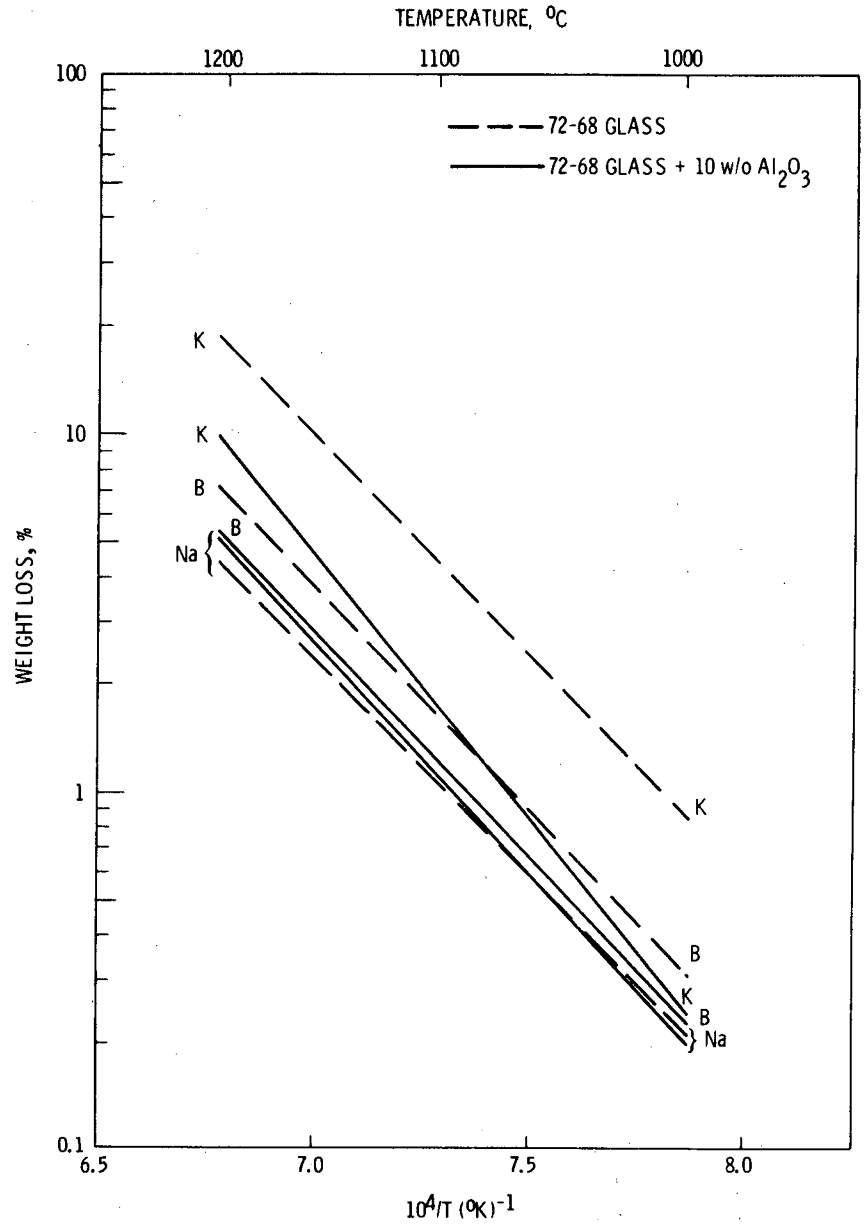

FIGURE 10. Fractional Weight Loss of Individual Elements After 4 Hr in Dry Air

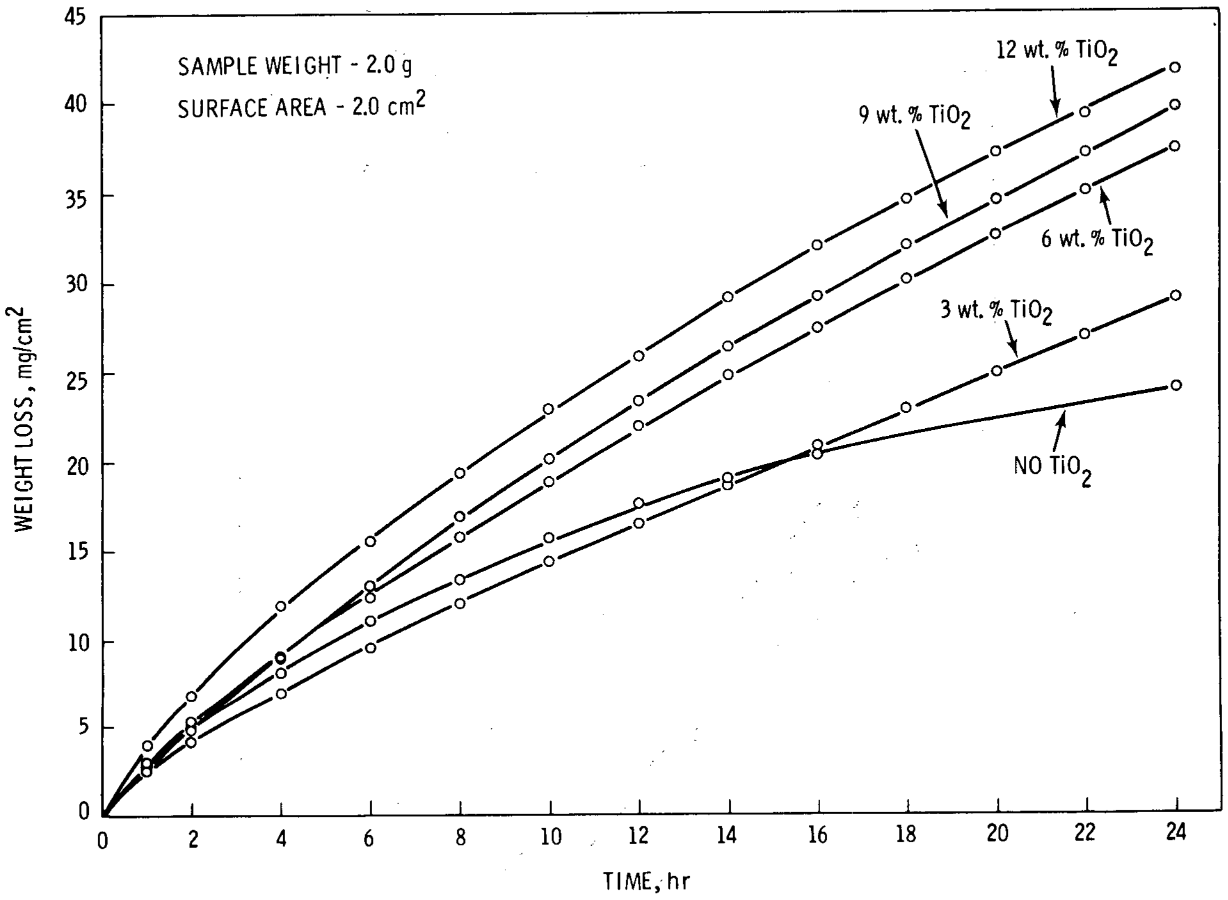

FIGURE 11. Weight Loss in Dry Air at 1100°C for 76-183 Glass Containing Various Amounts of TiO_2

TABLE 6. Percentage Weight Loss of Individual Elements From 76-183 Glass Containing Various Amounts of TiO_2[a]

Element	Weight Loss,%		
	No TiO_2	6 wt% TiO_2	12 wt% TiO_2
B	2.7	2.6	3.3
Na	0.6	0.7	0.7
K	5.2	6.8	8.0
Rb	7.0	7.8	9.1
Mo	0.8	0.8	1.1
Ru	14.6	18.8	43.6
Cs	14.6	18.9	24.2

(a) Samples were heated for 4 hr at 1100°C in dry air.

SECTION 3 - ALTERNATIVE WASTE FIXATION PROCESSES

The goal of this task is to develop alternative waste fixation procedures that will serve as viable backup processes. Cost and safety factors of the alternative processes and products are to be compared to those of the current reference process and product--silicate glass castings in large metal canisters. These alternative processes are being developed on the laboratory scale. In the concept currently emphasized the waste is formed into small granules or pellets that are coated with nonradioactive, inert materials to provide containment and leach resistance. The coated waste shapes are then incorporated into a metal matrix that provides impact resistance and increased thermal conductivity.

GLASS MARBLE DEVELOPMENT - J. M. Rusin

Corning Glass Works, Corning, New York, has a patented process for the vibratory forming of glass marbles.(a) The process is unique, in that a direct glass stream is used rather than the shearing of a viscous stream to form "gobs" of glass. Such a direct casting process would be adaptable to a remote facility. Discussions have been conducted with Corning to produce 1 to 4 tons of simulated waste glass marbles for process demonstration and to obtain large quantities of marbles for full-scale encapsulation. Corning has reviewed the feasibility of producing marbles from waste glass. Tests including crown and tank refractory corrosion and viscosity determination were made. In general, Corning found that marble production from simulated waste glasses was feasible. (They did observe platinum corrosion during the seven-day refractory test, which caused some concern.) But because of manpower and resource limitations, Corning cannot do the demonstration--at least not in CY 1978.

Production of glass marbles by the conventional process is also an option to obtain large quantities of marbles for encapsulation, even though the process is not readily adaptable to hot-cell operations.

THE PENNSYLVANIA STATE UNIVERSITY SUPERCALCINE INVESTIGATIONS - G. J. McCarthy, Program Leader

Leach Testing of Supercalcine - G. J. McCarthy and D. E. Pfoertsch

Because U-containing supercalcine (SPC) materials are not currently being handled at PNL, we have made Soxhlet leachability measurements on a batch of SPC-4 + U prepared according to the procedure described in the October-December 1977 Quarterly Report (McElroy et al., 1979). The -42+60 mesh powder was ground from 0.5-in. pellets that had been fired for 2 hr at 1225^{o}C. Three separate specimens of this SPC-4 + U were tested. Weight loss was monitored after 3, 7, and 14 days of leaching. In each case, more than 90% of the weight loss occurred in the first 3 days. After 14 days the leaching solutions were analyzed for Cs and Sr content. Leachability data expressed both as fraction extracted and in IAEA units are given in Table 7.

(a) U.S. Patent 3,254,979, "Method for Forming Balls from Thermo-Plastic Materials." Warren R. Knapp and Elmer R. Smith, assigned to Corning Glass Works, August 1962.

TABLE 7. SPC-4 + U Leachability in the 14-Day Soxhlet Test

	Fraction Extracted			Leach Rate, g/cm^2-day[a]		
Specimen	Bulk	Cs	Sr	Bulk	Cs	Sr
1	3.8-E3	3.3-E3	2.5-E3	8.4-E7	7.3-E7	5.5-E7
2	7.7-E3	1.4-E2	1.1 E2	1.9-E6	3.5-E6	2.8-E6
3	5.7-E3	5.2-E3	4.0-E4	1.7-E6	1.3-E6	1.0-E7

(a) Assumes 200 cm^2/gm surface area for the -42+60 mesh fraction. Specimen weights: 1 = 1.61g, 2 = 1.48g, 3 = 1.41g. In SPC-4, Sr = 3.6 wt%, Cs = 4.3 wt%.

Thermal Stability of Scheelite-Structure Solid Solution (Sss) Phases -

R. G. Johnston, D. E. Pfoertsch, and G. J. McCarthy

In the supercalcine formulations SPC-2 and SPC-4, Mo has been shown to be one of the primary waste species volatilized in part during prolonged high-temperature experiments. In supercalcine, Mo is incorporated into the scheelite-structure solid solution (S_{ss}), $(Sr,Ba,Ca)MoO_4$. Consequently, we have begun to examine the thermal stability of alkaline earth (AE) molybdate solid solution phases in order to ascertain the relationship between composition and thermal stability, both at supercalcine processing temperatures and at even higher temperatures.

We began by studying the pure end-members of the system: $SrMoO_4$-$BaMoO_4$-$CaMoO_4$. The weight loss behavior and stability of these oxides were examined by both dynamic and isothermal thermogravimetric analysis (TGA). Originally, commercial specimens of each phase, nominally of very high purity, were examined by TGA and XRD. All of these specimens showed some weight losses beginning at ∿800°C, with the largest being 7 wt% for $CaMoO_4$), and suggested that most or all of the weight losses were attributable to impurity phases. One would expect that any "free" Mo or Mo oxide (i.e., not combined in $AEMoO_4$) would begin to volatilize from the specimen at ∿800°C, near the melting point of MoO_3.

Phase-pure $CaMoO_4$, $SrMoO_4$, and $BaMoO_4$ were subsequently synthesized and the TGA measurements are now being repeated. Dynamic TGA (3.2°C/min) to 1320°C on each phase yielded only marginally detectable weight losses of 0.2 wt% or less.

The Ru Phase in Supercalcine -

R. G. Johnston and G. J. McCarthy

One of the long-standing questions in supercalcine crystal chemistry has been the phase in which Ru crystallizes. Because of the expense, a full loading of Ru (typically 3 to 4 wt%) is not included in SPC spray calciner runs. The 10% of this amount that is included means that the Ru phase would be present in crystallized SPCs at a concentration below the level of detection by XRD. A nearly pure Ru phase is observed in these products by metallographic and SEM/EDX techniques, but because of the metallic nature of RuO_2, it is not possible to distinguish between it and Ru metal. Recently, we added the full loading of Ru (as RuO_2) to both SPC-2 and SPC-4 spray supercalcines. After performing the usual air atmosphere crystallization-consolidation treatments on each, it could be clearly seen in high-sensitivity XRD diffractograms that the Ru phase in the ten-phase assemblage was RuO_2. This establishes that RuO_2 is the phase of Ru compatible with the other nine supercalcine phases during crystallization treatments in air.

Hot Pressing of SPC-4 - J. M. Bind

Samples of the as-received SPC-4 supercalcine were hot-pressed under the conditions listed in Table 8.

TABLE 8. Hot-Pressing Conditions for As-Received SPC-4 Supercalcine

Temperature, °C	Pressure, psi	Time, min.	Atmosphere
900	3000	75	vacuum
1000	3000	45	vacuum
1100	3000	40	vacuum
1200	3000	30	vacuum
900	3000	60	N_2
1100	3000	30	N_2

Average grain size of the powder was 6.7 μm; however, numerous large aggregates up to 53 μm were found. The hot-pressed samples were in the form of discs 3/4 in. in dia and about 3/16 in. thick. The hot-pressing time corresponds to the end of densification, which was indicated by the measuring equipment attached to the rams. As can be seen from the tables above, the higher the temperature, the shorter the time needed to achieve the final density.

Microstructural analyses were made with an SEM on fractured surfaces. Only the samples hot-pressed in vacuum have been characterized to date. Three general observations can be made:

- Samples hot-pressed below 1100°C contain an appreciable amount of porosity--especially the one fired at 900°C.
- The average grain size was about 5 to 10 μm, indicating that no substantial grain growth occurred during hot pressing.
- Some of the large aggregates of the original powder were found throughout the structure. They were always extremely dense, compared to the surrounding material, suggesting that they might have slightly different chemical compositions. Also, microcracking was noticed around these agregates.

SUPERCALCINE VAPORIZATION STUDIES - W. J. Gray

Supercalcine pellets 1.47 cm in dia x 0.37 cm high and weighing 2.0 g were prepared by cold pressing and sintering for 1 hr at 1100°C. The composition of the supercalcine (batch SPC-2) is given in Table 9. Volatility measurements on these pellets were conducted using equipment described earlier (Gray, 1976). The pellets were held in a platinum pan about the same height but slightly larger in diameter than the pellets for these studies.

TABLE 9. Composition of Supercalcine (SPC-2)

Waste Oxide	wt%	Waste Oxide	wt%	Additives	wt%
BaO	2.4	SrO	1.6	CaO	4.9
CdO	0.2	ZrO_2	7.6	SrO	1.2
Cr_2O_3	0.5	CeO_2	16.3	Al_2O_3	4.4
Cs_2O	4.5	La_2O_3	9.0	SiO_2	19.0
Fe_2O_3	4.7	Nd_2O_3	6.1		
MoO_3	8.0	Pr_6O_{11}	1.8		
Na_2O	0.2	Y_2O_3	0.1		
NiO	0.2	Sm_2O_3	1.1		
PO_4	4.2	Gd_2O_3	0.7		
Rb_2O	0.5	HO_2O_3	0.1		
RuO_2	0.5				

Gross weight-loss data were given earlier (McElroy et al., 1978) and are reproduced here in Figure 12 for completeness. The data are more scattered than has been found for other waste forms. Perhaps slight variations in density or surface area for the different pellets are responsible. The anomalously low points at 1150°C and 24 hr are reproducible, and these pellets came out a different color than at higher or lower temperatures. Apparently the formation or decomposition of some phase that results in lower volatility occurs after long time periods over a narrow temperature range.

Vapors were collected after 4, 12, and 24 hr at 1050°, 1150°, and 1250°C and were chemically analyzed. Each analysis was run only once; uncertainties, therefore, should probably be considered to be ±20% or ±30% of the values listed. Absolute weight losses of the individual elements during the first four hours and for the period from 12 to 24 hr are shown in Figures 13 and 14, respectively. Weight losses of the elements relative to the amounts originally present are shown in Figures 15 and 16. Finally, Figure 17 shows weight losses of elements from 72-68 glass (Gray, 1976) for comparison. Losses shown in Figure 17 are also relative to the amounts originally present. Several things should be noted about the data shown in Figures 13 through 17:

- On an absolute basis, Cs and Mo are the dominant elements in the vapor from supercalcine and are present in about equal amounts.
- Because Cs and Mo are the major elements in the vapor, their losses should be relatively low at 1150°C to account for the low total weight loss after 24 hours. Figure 14 shows this is the case, but all of the elements except Ru exhibit about the same behavior. Thus, there is no real clue here to suggest why the total weight loss at 1150°C and long times is so low.
- Relative losses of alkali elements from 72-68 glass (Figure 17) are in the order $Cs > Rb > K > Na$. In supercalcine the order is $Cs \simeq Rb < Na$. Perhaps this indicates that the heavier alkali alumino silicates are more stable.

- The relative losses of Cs and Mo are Cs >> Mo from 72-68 glass and Cs ≃ Mo from supercalcine.
- Gross weight-loss rates from supercalcine are roughly a factor of five less than from 72-68 glass, but Figures 15 and 17 show Cs volatility from supercalcine is a factor of about 25 less than from 72-68 glass.

Some x-ray characteristics were performed on supercalcine pellets that had been heated for 24 hr at 1100°, 1150°, and 1200°C. Differences observed between pellets occurred monotonically from the lowest to highest firing tempratures. That is, the percentage of crystalline phases and the number of different crystalline phases decreased more or less uniformly from 1100° through 1150° to 1200°C. Therefore, an adequate explanation for the anomalous behavior at 1150°C is still lacking.

Interestingly, 72-68 glass also exhibited anomalously low weight loss behavior at 1150°C (Gray, 1976). It seems strange for two such different materials to exhibit similarly anomalous behavior. But although it would be of academic interest to pursue this phenomenon, there are no plans to do so, as there is little practical incentive.

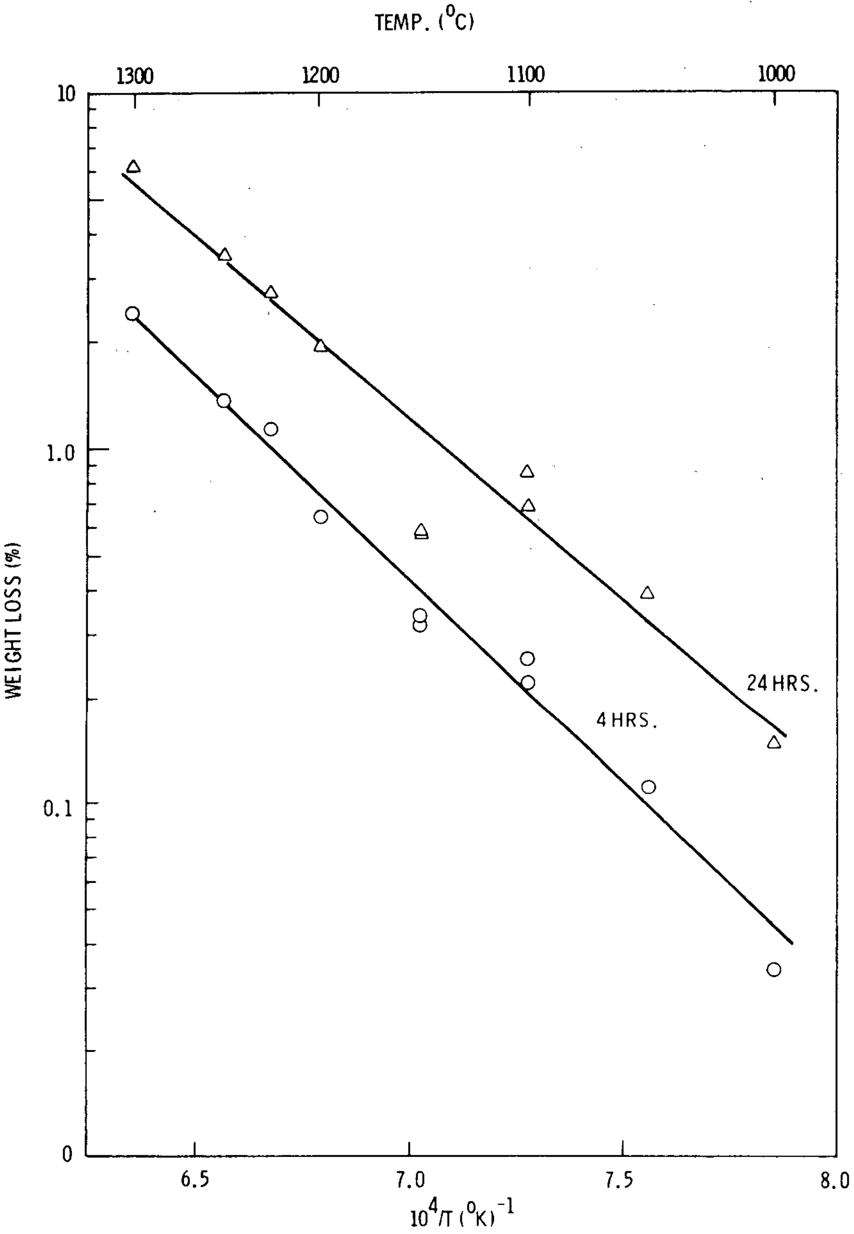

FIGURE 12. Weight Loss of Supercalcine (SPC-2) in Dry Air

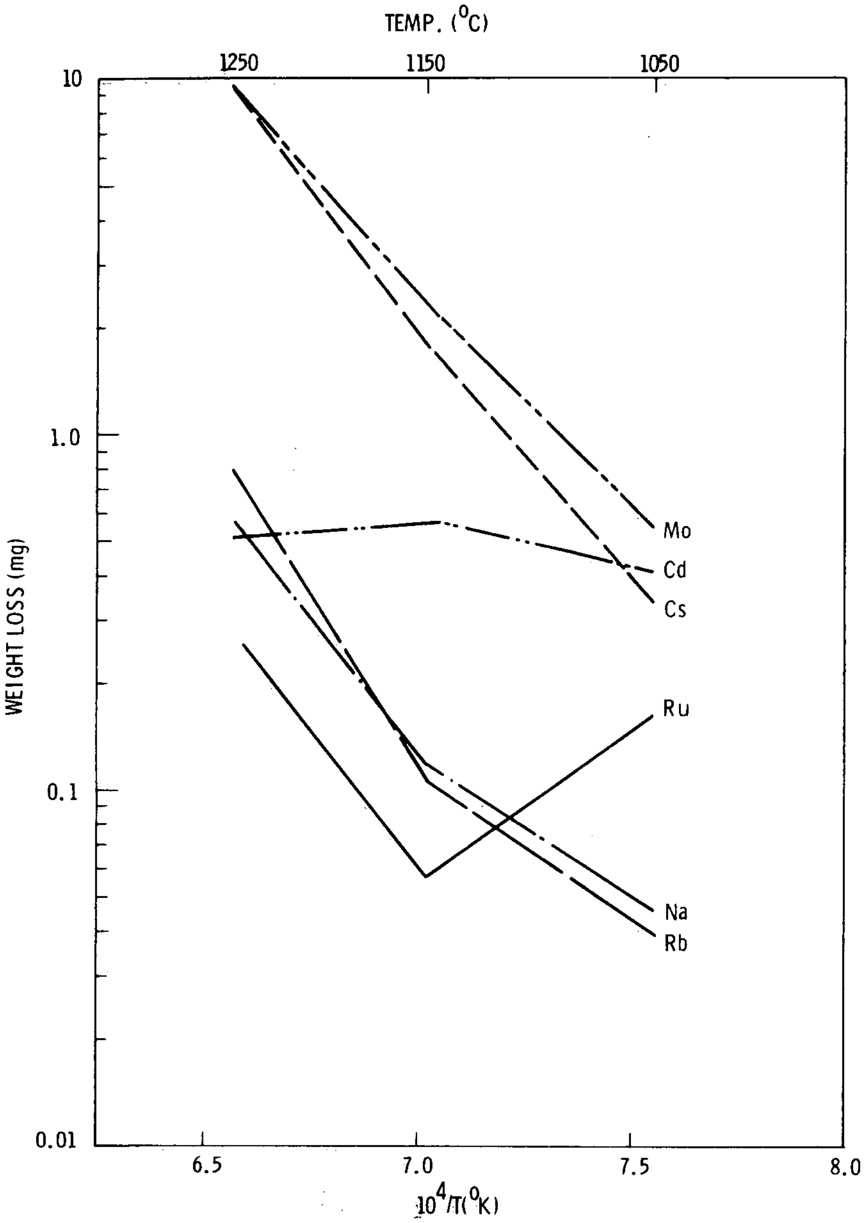

FIGURE 13. Absolute Weight Loss of Individual Elements from Supercalcine (SPC-2) After 4 Hr in Dry Air

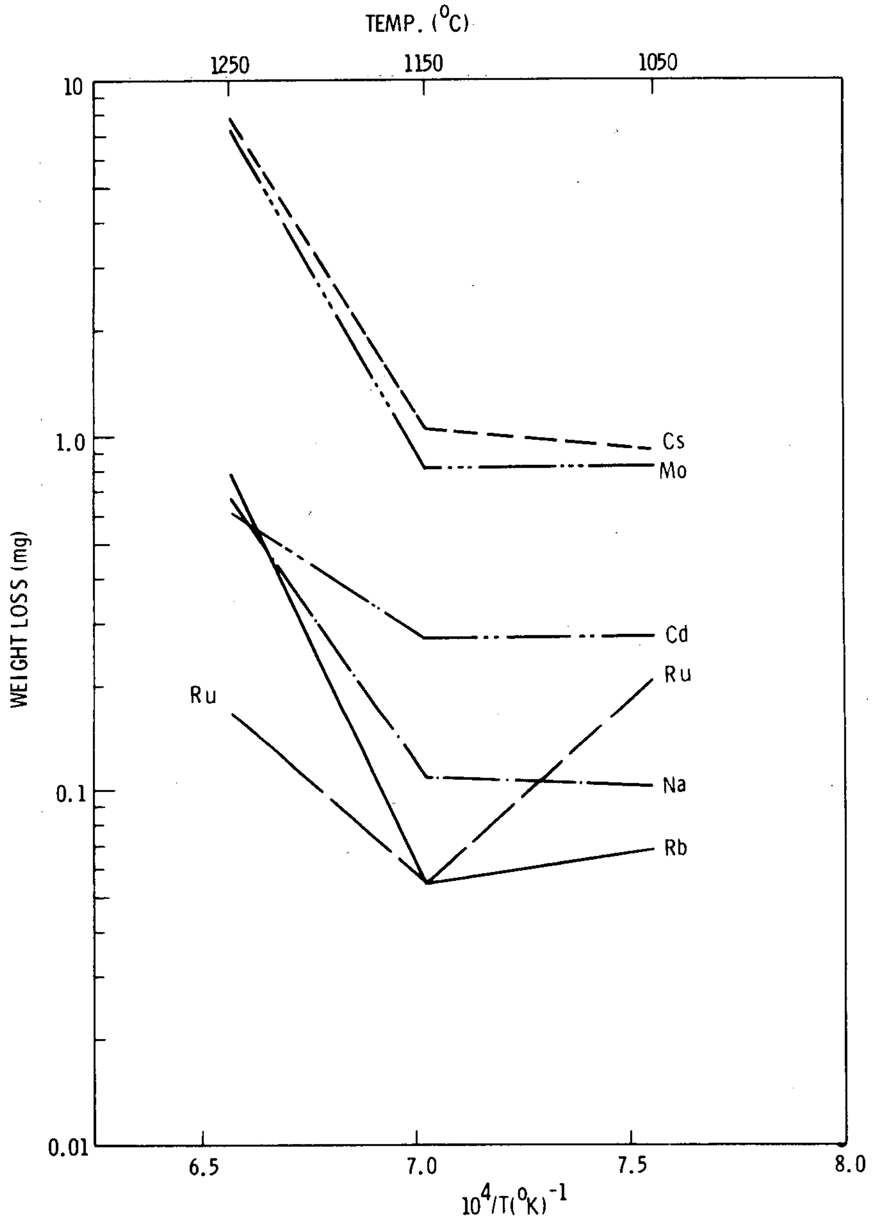

FIGURE 14. Absolute Weight Loss of Individual Elements from Supercalcine (SPC-2) During the Period from 12 to 24 Hr in Dry Air

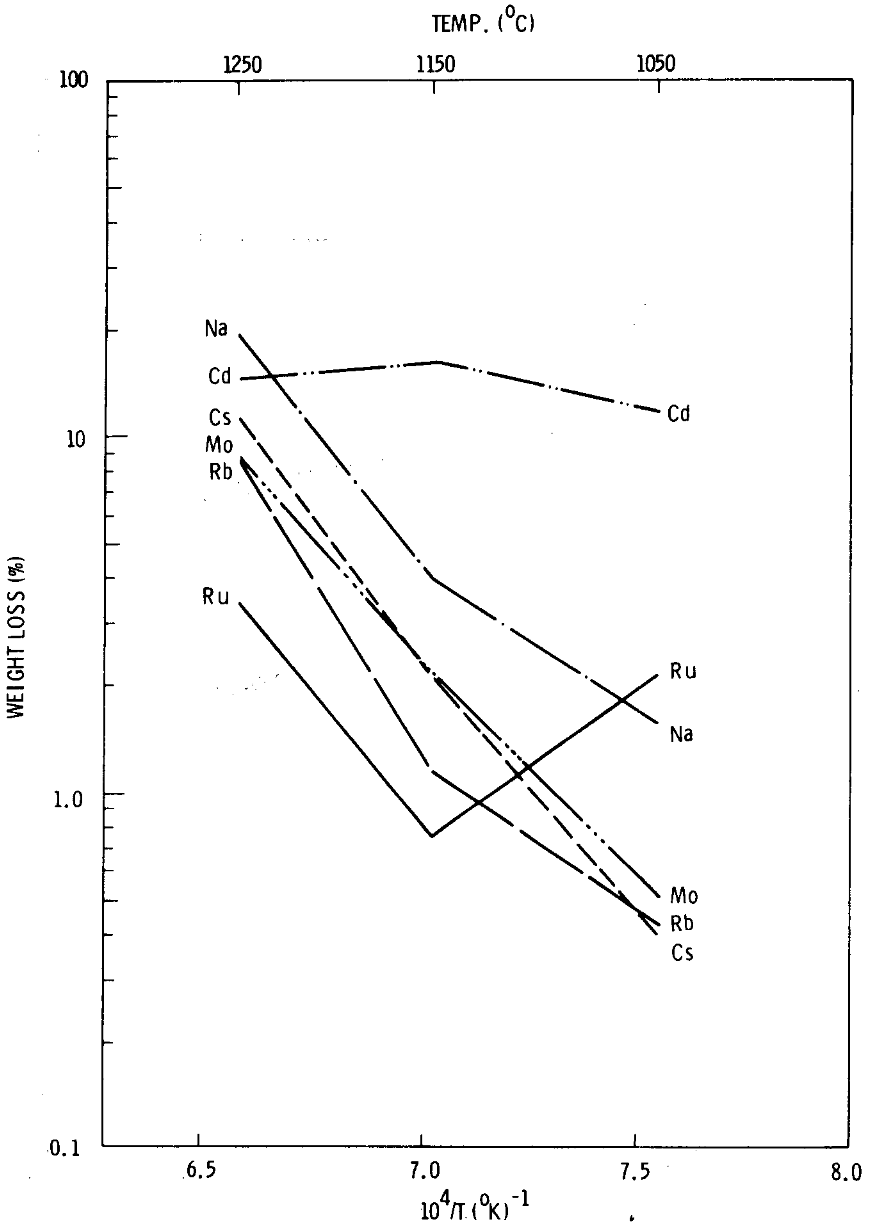

FIGURE 15. Fractional Weight Loss of Individual Elements from Supercalcine (SPC-2) After 4 Hr in Dry Air

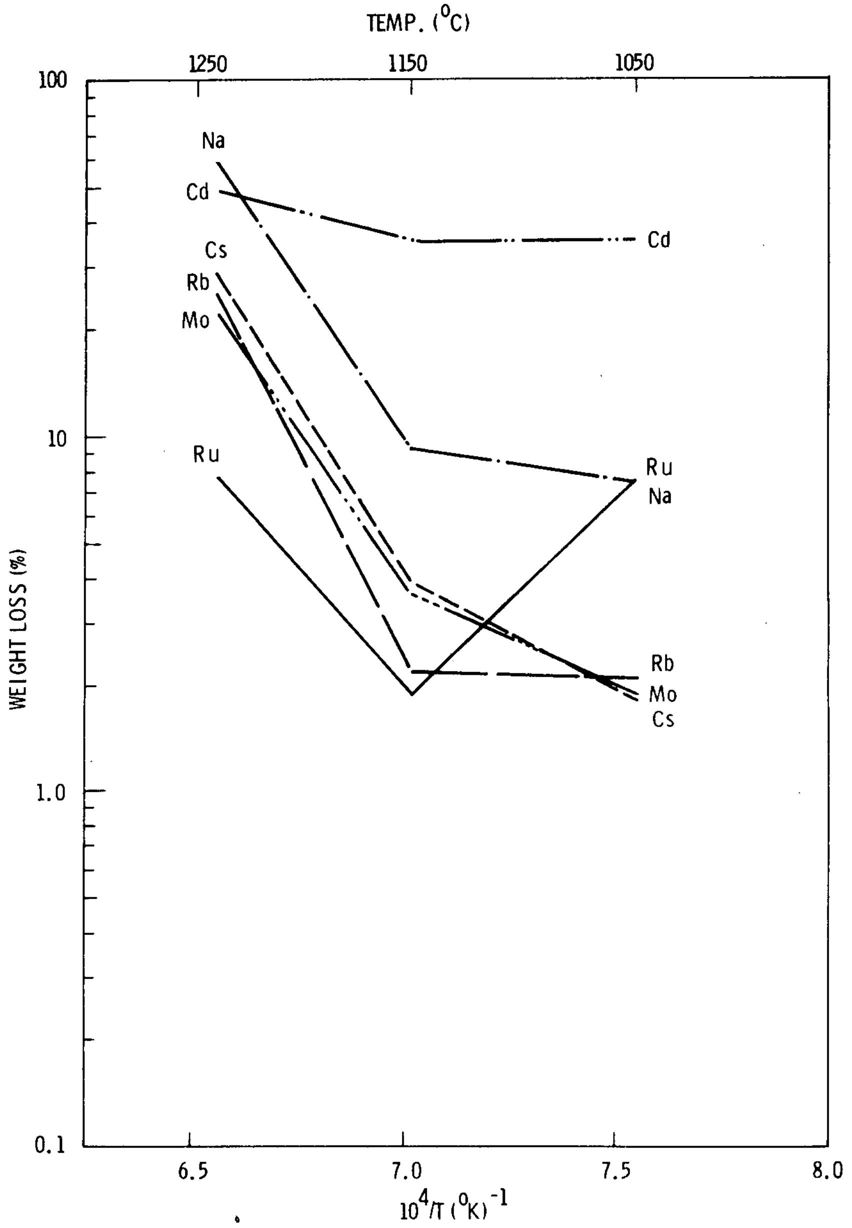

FIGURE 16. Fractional Weight Loss of Individual Elements from Supercalcine (SPC-2) After 24 Hr in Dry Air

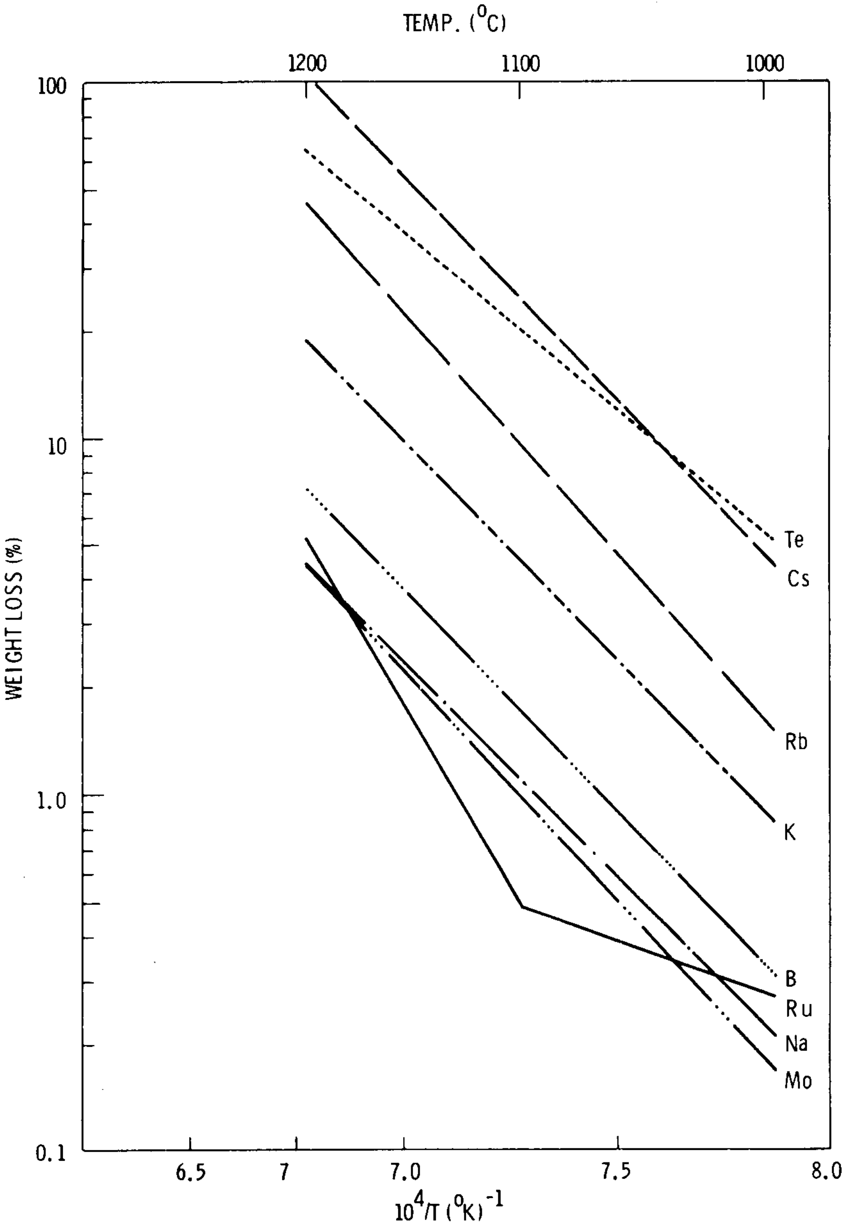

FIGURE 17. Fractional Weight Loss of Individual Elements from 72-68 Glass After 4 Hr in Dry Air

REFERENCES

Gray, W. J. 1976. Volatility of a Zinc Borosilicate Glass Containing Simulated High-Level Radioactive Waste. BNWL-2111, Pacific Northwest Laboratory, Richland, WA 99352

McElroy, J. L. et al. 1978. Quarterly Progress Report - Research and Development Activities - Waste Fixation Program: April Through June 1977. PNL-2265-2, Pacific Northwest Laboratory, Richland, WA 99352.

McElroy, J. L. et al. 1979. Quarterly Progress Report - Research and Development Activities - Waste Fixation Program: October Through December 1977. PNL-2265-4, Pacific Northwest Laboratory, Richland, WA 99352.

PNL-2999-2

HLWIP QUARTERLY REPORT
APRIL THROUGH JUNE 1978

PNL-2999-2
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QUARTERLY PROGRESS REPORT
RESEARCH AND DEVELOPMENT ACTIVITIES
HIGH-LEVEL WASTE IMMOBILIZATION PROGRAM: APRIL THROUGH JUNE 1978

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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 April through June of 1978:

- A new ceramic melter was coupled directly to the large-scale spray calciner. The results of initial tests showed the unit can produce in excess of 50 kg waste glass/hr.
- Several successful spray calciner runs were made in which all of the borosilicate glass batch was mixed with the liquid feed to the calciner, thereby simplifying the spray calcination/vitrification process.
- Waste glass leaching tests were performed at 350°C and approximately 2000 psi in salt brine and distilled water. In one week the reaction zones were 0.7 mm and >6 mm in salt brine and distilled water, respectively.
- Four 1-liter stainless steel canisters of four different multibarrier products have been produced to demonstrate feasibility of the multibarrier concept. Based on an assessment of processing complexity, glass marbles in a metal matrix are most promising; supercalcine particles coated with PyC/Al_2O_3 potentially have the most inertness, but processing is much more complex.

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 and -2999-1.

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APRIL THROUGH JUNE 1978

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 FIXATION PROCESS DEVELOPMENT

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

CERAMIC MELTER - C. C. Chapman, J. L. Buelt, R. D. Dierks

The calcine-fed ceramic melter (CFCM) has been coupled to the full-scale spray calciner and has been started up. A different technique for starting up a continuous melter was employed; it made use of silicon-carbide glow-bars in the melting chamber to melt a path between the two top entering electrodes. The CFCM was successfully started up in April. Testing with the unit has shown some problems in the section coupling the calciner to the melter. Glass-forming additives are sometimes melted and stick to the wall of the transfer pipe when the surface of the continuous melter is not more than half-covered by unmelted material. When in the incomplete cold-cap surface condition, the heat from the molten glass maintains the temperature of the transition pipe above the stick point of the frit and sticking to the walls occurs. Above a certain feed rate at which the plenum temperature is reduced by greater coverage of the molten glass surface, smooth operation results. Testing has shown the calcine-fed unit to have a capacity in excess of 50 kg/hr.

The LFCM continued to assess aqueous feeding, as well as simulated powder tests. Over 4000 kg of glass have been produced in the LFCM in the past quarter, and attention has been focused upon the removal of any residual sludges, a completion of ruthenium and cesium volatility tests for nitric acid solution without denitration, and the assessment of wear on the throat of the overflow section. Results of the ruthenium volatility are not back from chemical analysis. The measurement of throat wear after production of 2500 kg of glass in the LFCM by means of a feeler gauge was within the accuracy of the measurement device and suggested that little or no wear had occurred.

SPRAY CALCINATION - W.J. Mikols

Progress this quarter has been marked by the completion of nine spray calciner runs. Of these nine, five runs were made using large-scale spray calcination equipment. The objectives of these large-scale runs included system demonstration using cyclone separation, spray calcination of Savannah River Plant high-iron and high-aluminum feeds, and demonstration of a calciner/ceramic melter-coupled system.

The remaining four runs were made on pilot-scale equipment. The main emphasis of these runs was to demonstrate the feasibility of spray-calcining complete glass batch compositions. Development of this concept will considerably simplify the spray-calcination/vitrification process.

IN-CAN MELTING DEVELOPMENT - H. T. Blair

Five tests were made in the pilot-scale in-can melter using spray-calcined simulations of the defense wastes stored at Savannah River and frits developed at the Savannah River Plant (SRP).

The results showed that these glass compositions foamed when melted and that this foam reduced the melting rate that could be sustained.

In the last report we presented the criteria for a remote connecting section and for canister support and a weighing system. During this quarter a concept was conceived that would satisfy these criteria by adequately aligning a bottom-supported canister to facilitate spout engagement and to allow for thermal expansion without interfering with the in-process weight monitoring of material delivered to the canister. The concept mechanically isolates vertical alignment of the canister from the furnace by means of an external, cradle-like frame, and provides a "floating" spout in the connecting section to accommodate the tolerance of canister alignment. The cradle-like frame connects the canister support base with guides located near the opening in the furnace. A combination cover/locking collar is engaged with the existing twist-lock opening of the canister prior to lifting the canister to the furnace. As the assembly is lowered into the furnace, the cover engages the guides to center the canister on the support base and to limit canister tilt. Because the canister, cradle-frame, and cover/locking collar are weighed, canister position and/or tilt do not affect weight measurements. The locking collar guides and centers the "floating" spout with respect to the canister seal. The spout is weighted to provide the desired sealing force. Flexible joints and bellows in the delivery tube of the connecting section accommodate the "floating" spout, extension and retraction of the spout, and thermal expansion of the connecting section and canister. The spout-valve actuator is mounted to the frame of the "floating" spout, and thereby maintains a seal with the spout independent of spout movement. A combination expansion and swivel joint is located between the diverter and the delivery tube to accommodate expansion of the calciner and to permit the connecting section to be rotated to one side so that canisters may be exchanged in the furnace.

Detailed design work was started on a connecting section to demonstrate the technical feasibility of the concept described. This demonstration hardware is being designed for use with the full-scale spray calciner/in-can melter system at PNL. A schedule was established for completing the design, having the equipment fabricated, and installing it, so that a demonstration may be performed in March, 1979.

Five in-can melting tests were made in the pilot-scale melter using spray calcined, simulated wastes and frits of various compositions specified by Savannah River Laboratories. The runs are summarized in Table 1. The main objectives of the tests were to evaluate the melting behavior of these compositions and to determine the maximum melting rate that would be sustained in a reference ICM setup for comparison with previous results.

The cans and fin assemblies used for the tests were all of the same design and size. Only the can wall material was varied to permit melting at 1150°C. Because defense wastes produce low levels of heat generation, the gap between the edges of the fins and the can wall could be reduced from the 1/2-in. gap used for commercial wastes; this smaller gap adequately assures an acceptable heat distribution on the surface of cans containing defense waste.

The results of these tests showed that the significant melting characteristic of these batch compositions, as far as process equipment was concerned, was the evolution of gas after

TABLE 1. Summary of In-Can Melting Sums SRP ICM-3, 4, 5, and 6

	Run Number and Characteristics				
Information Summary Categories	SRP ICM-3	SRP ICM-4	SRP ICM-5a	SRP ICM-5b	SRP ICM-6
Run					
Date of Run	5/16/78	5/18/78	5/22/78	5/22/78	5/25/78
Coupled to	Vibra-Screw Feeder	Vibra-Screw Feeder	Vibra-Screw Feeder	Same as 5a	Vibra-Screw Feeder
Off-Gas Treatment	Pilot Spray Calciner	Pilot Spray Calciner	Pilot Spray Calciner	Same	Pilot Spray Calciner
Canister					
Diameter, in.	8 Schedule 10S	8 Schedule 10S	8-3/8 I.D.	Same	8 Schedule 10S
Length, in.	60	60	60	Same	60
Wall Thickness, in.	0.148	0.148	0.125	Same	0.148
Material	304L SST	304L SST	Inconel-601	Same	304L SST
Fins	8 (36 in. long)	8 (36 in. long)	8 (36 in. long)	Same	8 (36 in. long)
Batch					
Waste Type	TNX Sludge	No Na Composite	No Na Composite	Composite	Composite
Waste Form	Spray Calcine FSSC-9	Spray Calcine FSSC-11	Spray Calcine FSSC-11	Spray Calcine FSSC-10	Spray Calcine FSSC-10
Waste Oxide-to-Frit Ratio	1:1.87	1:3	1:3	1:1.87	1:1.87
Frit Type	SRP 21B	SRP 21	SRP 21	SRP 21B	SRP 21B
Frit Form, mesh	-10/+80	-20/+80	-20/+80	-20/+80	-20/+80
Additives	None	None	None	None	None
Batch Preparation	Mixed	Mixed	Mixed	Mixed	Mixed
Operating Parameters					
Time at Melt Temperature, hr	9-1/2	11-1/2	13	Same	9-1/4
Surface Temperature Range, °C	1045 to 1055	1050	1090 to 1155	Same	1045 to 1055
Nominal Melt Temperature, °C	1050	1050	1130 to 1150	Same	1050
Batch Feed Method	Continuous(a)	Continuous(a)	Continuous(a)	Same	Continuous(a)
Max. Batch Feed Rate, kg/hr	21	38.6	17.8	19.5	7
Melting Rate, kg/hr	12.5	10.5	17.8	14 to 17	7
Max. Power Consumption, kw	21	20	36	23	15
Glass Cooling Rate, °C/hr					
1025°C to 750°C	55	57	53	Same	69
750°C to 500°C	Air Quenched	Air Quenched	Air Quenched	Same	67
500°C to 100°C	Air Quenched	Air Quenched	Air Quenched	Same	Air Quenched
Product					
Type	TNX (1:1.87)21B	No Na Comp. (1:3)21B	No Na Comp. (1:3)21	SRP Comp. (1:1.87)21B	SRP Comp. (1:1.87)21B
Weight, kg	57.5	58.7	53.6	Same	18.6
Volume	22.7	23.2	21.0	Same	7.4
Bulk Density, g/cc	2.53	2.53	2.55	Same	2.52

(a) Rising level melt

the batch had become a melt but before the viscosity of this melt was low enough to expedite the release of the gas from the melt (i.e., these batch compositions foamed as they melted). The foam reduced the rate at which batch could be melted by acting as an insulating layer between the heated surfaces of the can and fins and the materials to be melted. It also rapidly filled the volume of the can where melting was to take place. The fins helped in rapidly dissipating the foam by improving heat transfer into it, so that the recovery from an over-foamed condition took only 15 to 30 minutes after batch charging was stopped. Operating the melter at higher temperatures improved the rate of foam dispersal, but the rates sustained were still only 60% of the 30 kg/h routinely achieved with batch compositions that release all volatiles before they melt. Reducing the viscosity of the melt with respect to the melting temperature also improved the melting rate, but this effect will be limited by the fact that the escaping gas must always pass through the surface of the melt where fresh batch is keeping it cool and viscous. To take advantage of this effect of a compositional change, the batch should be charged intermittently so that the surface may become heated and fluid.

The first three cans were cooled in the furnace to between 755°C and 770°C, and were then removed from the furnace and air-cooled in a wire mesh cage to collect the spall. We collected 360 g of spall from the outside surfaces of the can used for run SRP ICM-3 and 107 g from the can used for run SRP ICM-4. No spall fell from the can that was made from Inconel-601. Why the large difference between the amounts of spall collected from the two steel cans is unknown. The outside surface areas and process temperatures were the same for both cans, and the process times were not significantly different.

EFFLUENT CONTROL - M. S. Hanson

A sintered stainless steel filter that had been used to separate calcine from the system off gas was destructively tested to find out if ruthenium was plating out internally in the filter. If the phenomenon occurred, the deposition of ruthenium in the filter could increase the filter pressure drop. Microprobe analysis of the cross section of the filter showed no concentration points of ruthenium. The analysis found no ruthenium in concentrations greater than 0.5% in any 1-μm-dia spot.

BATCH/PROCESS CHEMISTRY - J. M. Lukacs, C. C. Church

Spinel Crystal Size and Volume Distribution--SRP "Average" Glass

This quarter we examined two samples of SRP "average" waste glass melted at 1100°C for 1 hr and 158 hr to determine the size and volume distributions of the $NiFe_2O$ spinel phase. Micrographs of these samples were included in the last quarterly (McElroy, Mendel, Bonner and Henry 1979). Results as determined by a Quantamet Image Analyzer are summarized in Table 2. The crystal regions in the 158-hr sample were divided into two sections to separate the smaller number of large crystallites (Area A) from the bulk of the crystallites that had settled from the glass.

Crystal size and volume distributions were comparable for 1-hr and 158-hr samples. Holding the sample for 158 hr at operating temperature increased the crystal loading near the

TABLE 2. SRP-1 "Average" Waste Glass

Characteristics Studied	Melting Time 1 hr	Area A 158 hr	Area B 158 hr
Volume% Crystalline Phase	4.1 ± 1.0	17.8	14.3 ± 3.0
Average Crystal Dia (μm)	8.6 ± 1.3	17.4	8.0 ± 1.1
Median Crystal Dia (μm) (based on dia)	8.2 ± 1.2	12.0	7.3 ± 1.4
Median Crystal Dia (μm) (based on vol)	13.5 ± 1.5	55.0	14.7 ± 1.5
Maximum Crystal Dia Observed (μm)	23.2 ± 1.6	75.0	30.3 ± 6.3
Number of Features Measured For Distribution Data	1440	141	1616

bottom of the crucible from approximately 4 vol% up to 14 vol%. Although a few large crystals were observed after 158 hr, the majority of crystals did not exhibit significant growth.

Product Evaluation During Melter Operation

During the period 3/9/78 to 4/19/78 we collected glass samples from the overflow during melter operation. Over 8000 kg of simulated waste glass were produced. Initial results indicate that this sampling technique is suitable for monitoring glass properties and composition. Reliable composition data were produced by x-ray fluorescence analysis for the heavier atomic constituents. It was possible to monitor glass properties such as density, viscosity, microstructure, and leachability as a function of melter operating time and glass composition.

Idaho National Engineering Laboratory (INEL) Melter Development Program

A preliminary program to characterize INEL-developed waste glass has been initiated. The results will determine whether the defined glasses are compatible with in-can and continuous melting processes.

CANISTER DEVELOPMENT - S. C. Slate

One of the most important objectives of this work is a reference design and a detailed description of all the processing operations for waste storage canisters. To achieve this objective we have made analytical studies, created conceptual designs for processing equipment, and have tested full-scale canisters. A draft report was prepared this quarter that describes PNL reference canister designs and the processing operations from fabrication through transportation to disposal. This report will be routinely updated as our work progresses and will be issued at a later date.

We discuss the designs and processing operations for canisters used in both the in-can melting (ICM) and continuous melting vitrification processes. Both processes have several different requirements for the canisters.

From preparing this draft report we have concluded that the design or processing of waste canisters is not limited by major technical problems. Once the specific requirements for the overall waste management systems have been established, a highly reliable waste canister can be designed and used.

SECTION 2 - WASTE FORM CHARACTERIZATION

The purpose of waste form characterization is to measure the properties of candidate solidified products and containers (solidified waste and canister) as functions of composition, processing parameters, and storage conditions. The measurements are used to: 1) ensure operability of the vitrification processes and 2) provide data for safety analyses of high-level waste management. The ultimate goal of waste characterization 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 a final disposal site, we may be fully confident that their behavior is understood and that any changes or interactions with their environments are wholly predictable.

ENVIRONMENTAL REACTIONS OF WASTE GLASSES - J. H. Westsik, Jr.

ISO Soxhlet Leach Test

A proposed standard Soxhlet leach test procedure has been written and forwarded to the International Standards Organization (ISO) for their consideration. The procedure calls for leaching a block of waste material for 72 hr in continuously redistilled water. Weight loss is used to calculate the leach rate in kg/m^2. The apparatus includes a glass condenser, a round-bottom flask, and a commercially available Soxhlet extractor.

Concentration Effects on Leachability

Waste glasses can withstand large variations in the frit-to-calcine ratio without losing leach resistance. However, changes in leach rates caused by variations of individual fission product concentrations have not been determined. We found that in the range from 0.5 to 5.0 times the defined cesium and strontium concentrations, leach rates remain constant.

Samples of 76-68 glass in which the cesium and strontium concentrations deviated by ratios of 0.1, 0.5, 1.0, 2.0. 5.0, and 10.0 from the defined concentrations were leached using the modified IAEA method. The average leach rates based on cesium from 7 through 119 days are plotted in Figure 1. In the range from 0.5 to 5.0 times the defined concentrations, leach rates remain constant. This means that more ion is released from the higher-concentration glasses, but that the fraction released of the total amount of the ion in the glass remains constant. When the ion concentrations vary by a factor of >10 from the defined amount in the glass, the leach rates increase significantly.

High-Temperature and High-Pressure Leachability

We are studying the hydrothermal reactions of 76-68 [PW-8a-3(1:2)76-101] glass. Powdered glass and a solid core were heated together at 350°C in deionized water for one week. Powdered salt and -100 mesh 304 stainless steel were added to the system to determine their effects upon the reaction products. The ratio of glass to salt to water was 1:10:12.5. Table 3 shows the leach rates based on weight loss of the glass cores.

Metallographic examination of the cores revealed that the two exposed to salt brine developed a reaction zone 0.7 mm thick as shown in Figure 2. Figure 3 reveals that the core

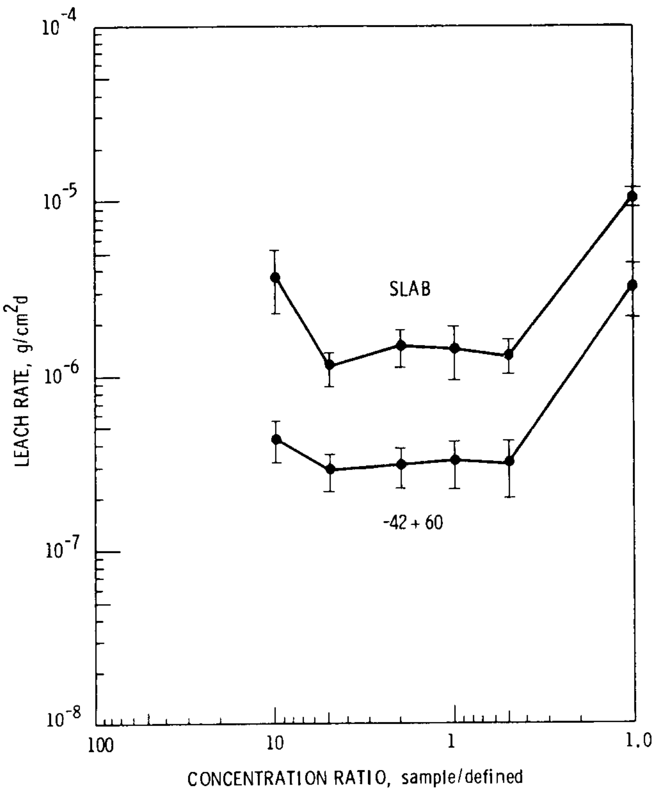

FIGURE 1. Leach Rates of 76-68 Glass Based Upon Cesium as a Function of the Cesium Concentration in the Glass

TABLE 3. Hydrothermal Glass Reaction Results

Test Number	Test Constituents	Leach Rates
Test 2	glass + salt + steel + water	4.0×10^{-3} g/cm^2-day
Test 3	glass + salt + water	4.7×10^{-3} g/cm^2-day
Test 4	glass + water	5.3×10^{-3} g/cm^2-day

exposed to deionized water reacted through its entire 13-mm diameter. Figure 4 shows the concentration profile through the reaction zone. of the sample treated in salt brine. X-ray fluorescence of the core surface and chemical analysis of the leach solutions show that cesium, rubidium, and molybdenum are removed from the glass surface in salt brine and that more is leached from the glass in salt brine than in deionized water.

From the data we conclude that the canister material does not affect the hydrothermal reaction. Salt inhibits the rate of alteration of the glass, but it increases the amount of cesium released.

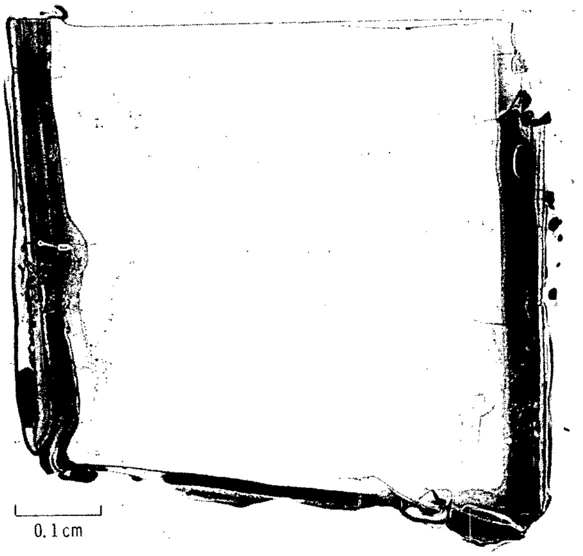

FIGURE 2. Reaction Zone in 76-68 Glass Exposed to Salt Brine at 350°C

FIGURE 3. Reaction Zone in 76-68 Glass Exposed to Deionized Water at 350°C

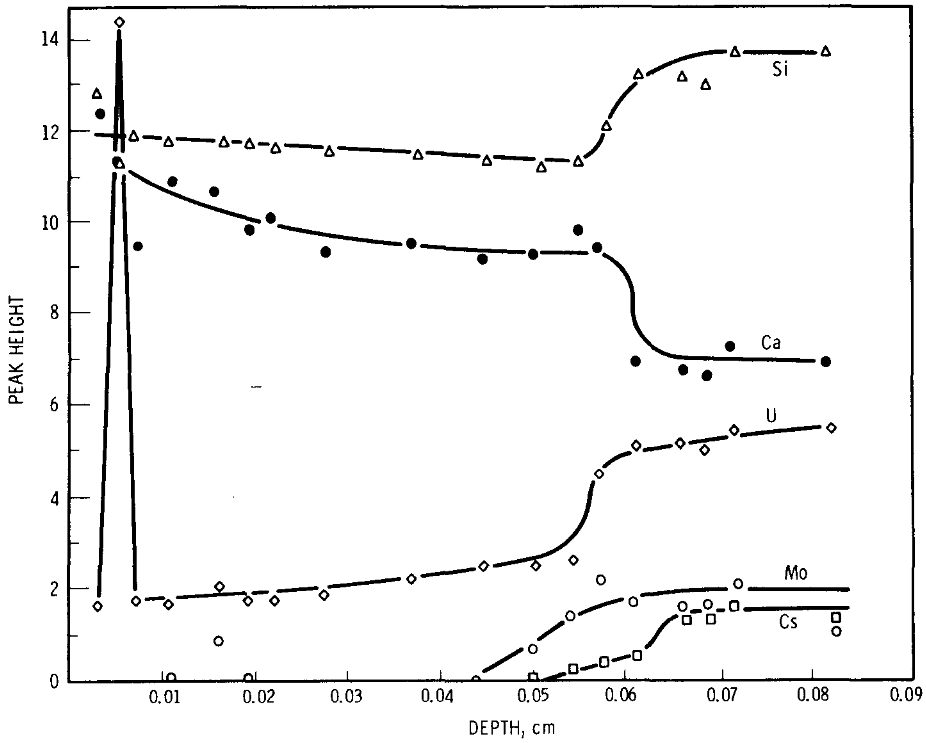

Figure 4 Concentration Profile through the Reaction Zone of Glass Exposed to Salt Brine

FULL-SCALE CANISTER IMPACT TESTS - S. C. Slate

In December 1977 impact tests were conducted using full-scale canisters containing simulated waste glass. Data from these tests have been analyzed and compiled into a draft report this quarter. The purpose of these tests was to evaluate the behavior of a waste canister that was impacted during a handling or transportation accident. Earlier impact tests at PNL were primarily concerned with characterizing the effect of the impacts on the glass (Smith and Ross 1975).

A total of thirteen canisters were tested. These canisters ranged from 12 in. to 24 in. in dia and they were dropped from heights ranging from 20 ft to 100 ft. The test pad consisted of a 7-in.-thick steel plate set in a 4 x 4 x 10 ft concrete block. No canisters that were built according to the reference PNL design failed in any of the tests. Only one non-prototypic canister released glass after it was dropped two times from thirty feet. We have concluded from these tests that canisters can be simply designed to sustain severe impacts to the bottom or sides. Further tests will be necessary to demonstrate the impact behavior of current canister-top designs. Specific results from these tests will be published at a later date.

THERMAL AND MECHANICAL SHOCK - L. R. Bunnell

In order to evaluate the increase in surface area caused by internal cracking of simulated waste-containing glasses poured into large (up to 36-in.-dia) canisters by the ceramic melter, samples were subjected to sieve analyses. Some typical results presented in terms of screen size vs cumulative weight percent are shown in Figure 5. The log-log paper is

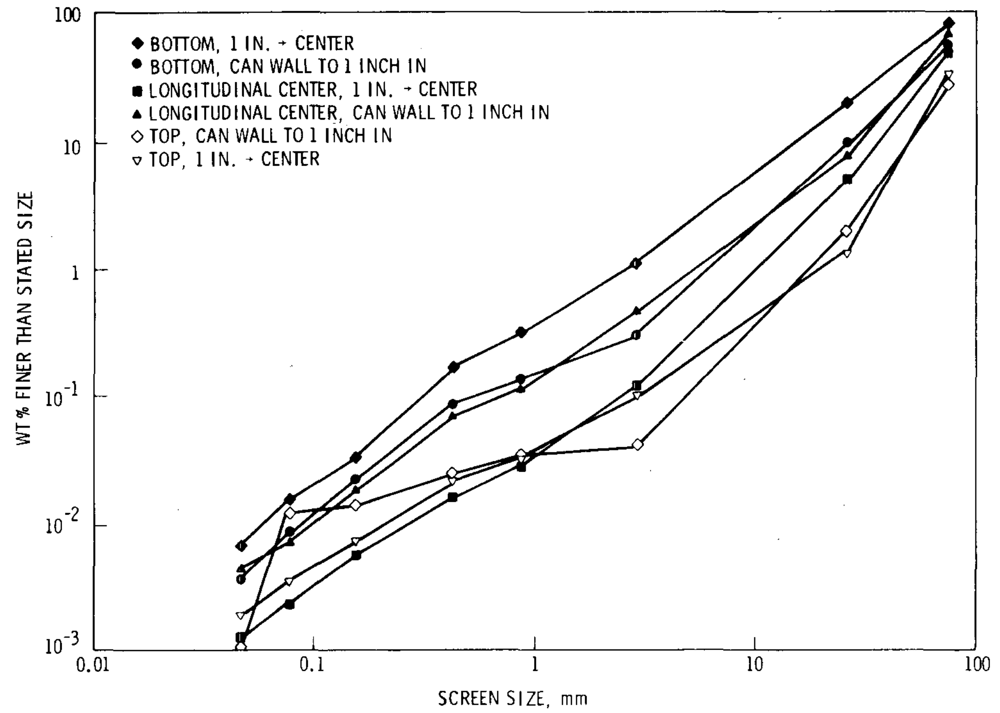

FIGURE 5. Particle Sizes Observed in an As-Fabricated 36-in.-dia Waste Canister--Run 2-H

used only to span the necessary decades; no exponential relationship is necessarily implied. If the size information is used to calculate the increase in surface area over and above geometric surface, the ratios in Table 4 result. These are for a 36-in.-dia can from run 2-H. The highest surface area is created at the bottom of the canister, presumably because the quench conditions during pouring are the worst there. The area ratios at each end are altered by considerations of the end, which is why those are lower than in the middle of the canister. Similar calculations will be done with data from several other cans.

Glass composition 77-260 containing 2 wt% ^{244}Cm was impacted at 160 ft-lb. The glass was prepared in three different states of crystallinity by controlled cooling from the melt. Figure 6 shows the sieving results, and includes an identical soda-lime-silica glass specimen impacted under the same conditions. At least in the +37 μm size range, it appears that all of the glasses are similar to and slightly better than soda-lime-silica glass. Furthermore, they are all similar to each other. Both of the devitrified glasses appear to be slightly better than the vitreous, but differences are small. The possibility of doing sedimentation size analysis on the fine material (-37 μm) is being examined. These same glass types will be impacted again after the curium has produced self-damage in the glass.

TABLE 4. Calculated Surface Area Ratios for 36-in.-dia Canister 2-H

Location	Calculated Surface Area, cm^2/g	Ratio to External Surface Area
Bottom	1	9.4
Middle (Longitudinal)	0.5	27.6
Top	0.5	5.9

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

An experiment to "quantitatively" show the relative changes in microstructure and other properties of the 77-260 waste glass composition caused by radiation damage has been undertaken. The radiation damage in this experiment will be induced by the alpha decay of ^{244}Cm, which is added as a dopant to the waste glass. This study will involve the cooperative effort of several contributors in order to measure and evaluate the changes in microstructure, density, stored energy, leach rates, and impact strength that result from radiation damage.

As a preliminary step in this experiment, samples of 77-260 waste glass were doped with terbium instead of curium. This preliminary experiment served to identify problems in sample preparation and to characterize the microstructure of the glass types to be studied.

Waste glass 77-260 has now been doped with 2 wt% ^{244}Cm to induce damage by alpha decay. Three glass types that typify potential states of devitrification have been prepared from the doped glass. The three glass types and the treatment each received are as follows:

1. devitrified at 700°C for 1 week to produce a uniform dispersion of very fine crystals
2. devitrified by slow cooling from 1050°C at -6.25°C/hr to produce a dispersion of large crystals
3. vitreous (except for clusters of RuO_2 and palladium metal).

The above glasses have been distributed to all contributors for property measurements and evaluation.

Initial results at relatively low fluences (1.5×10^{17} α/g) indicate that the density change in both devitrified glasses is in the negative direction. No significant change has been observed in the density of the vitreous glass. In addition, no changes have been observed in the x-ray diffraction patterns of the three glass types at this early stage of the experiment.

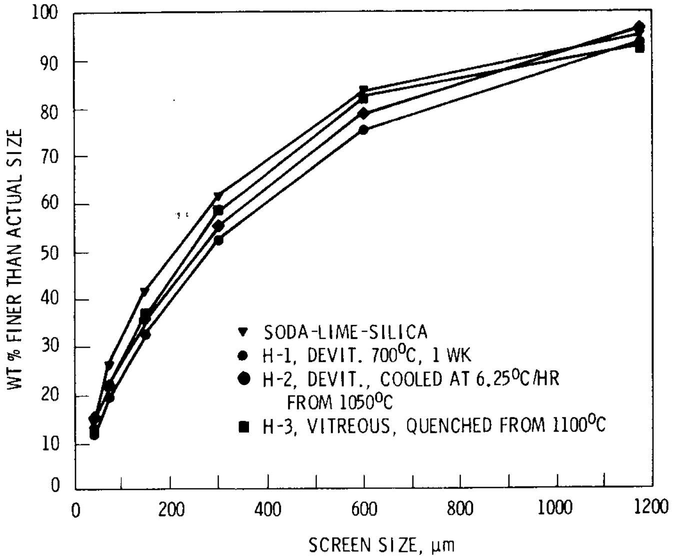

FIGURE 6. Particle Sizes Produced by a 160 ft-lb Impact on ^{244}Cm-Loaded Glass, Compared to Soda-Lime-Silica

PHASE BEHAVIOR - R. P. Turcotte and J. W. Wald

Detailed studies of a high-sodium, high-iron glass composition (76-68) are nearing completion, including anhydrous devitrification studies for periods up to one year and some hydrothermal work at 350°C.

Anhydrous Devitrification

Table 5 summarizes our understanding of devitrification in glass 76-68 after isothermal treatments at between 300° and 1000°C for up to one year. The major phase found after the 1-yr treatment is $NaFeSi_2O_6$, reaching ~30 wt% at 750°C. At 600°C and lower temperatures, no significant increase in crystallinity was observed over that present at the time of vitrification (~6 wt% total, RuO_2, Pd, $NiFe_2O_4$).

TABLE 5. Crystalline Phases Present in Glass 76-68

Phase	Description
$(Ce,U,RE)O_2$	Fluorite structure type, exists 1 da → 1 yr, max. conc. @ ~2 wt%
$NiFe_2O_4$	Primary spinel, exists 1 da → 1 yr, max. conc. ~5 wt%
RuO_2	Melt insoluble, conc. ~2 wt%
$NaFeSi_2O_6$	Major devit. phase, appears after 60 da, max conc. ~30 wt% after 1 yr
$CaMoO_4$	Minor phase/trace, exists 1 da → 1 yr
$(Ce,RE)PO_4$	Monazite mineral type--SEM indicates trace presence @ 1 yr time, x-ray verifies

Hydrothermal Alteration

The 76-68 glass composition is also being studied under hydrothermal conditions in salt brine. The objective of this work is to define alteration kinetics, establishing both the composition/structure of solid products and defining elements that may enter the solution phase. At 350°C the reaction is quite rapid, with $NaFeSi_2O_6$ being the major alteration product, as also found after long-time, high-temperature treatment under anhydrous conditions. X-ray fluorescence analyses of completely reacted glass powder shows that only cesium, rubidium, and molybdenum are leached in measureable quantities. Strontium and 15 other elements analyzed for remain as solid products in phases yet to be identified.

GEOLOGIC MATERIALS: IMPLICATIONS FOR RADIOACTIVE WASTE DISPOSAL -

R. C. Ewing, University of New Mexico

A detailed report of the long-term stability of naturally occurring glasses (volcanic glasses, tektites, and lunar glasses) has been completed and submitted to PNL for review. The report details the age distributions of these natural glasses, as well as alteration, devitrification and hydration effects.

Volcanic glasses, the most common of the naturally occurring glasses, are very often altered by weathering and leaching (crystalline phases may show similar effects) and recrystallize to their fine-grained compositional equivalents (rhyolites and felsites). The oldest reliably dated volcanic glasses are 40 million years old, but the majority of the dated glasses are much younger. Experimental studies of volcanic glasses have produced devitrification textures; and laboratory experiments, as well as empirical measurements, have determined hydration rates for volcanic glasses as a function of composition, temperature, and climate. The presence of water and the temperature are the most important rate-controlling variables. Even material that still may be described as glassy often exhibits evidence of alteration and recrystallization. Of the volcanic glasses that are preserved in the geologic record, few may be described as pristine.

Despite the common alteration and recrystallization effects observed in volcanic glasses, tektites and lunar glasses (which are glasses formed as a result of impact) may occur in a substantially unaltered form. In the case of tektites, their resistance to alteration is a result of their high SiO_2 content and low alkali content. Lunar glasses have been preserved for hundreds of millions of years because they exist in an environment with a low oxygen fugacity and at extremely low water vapour partial pressures. Thus, one might expect glasses of particular compositions or in specific types of environments to be stable for long periods of time.

It is difficult and inappropriate to make direct comparisons between naturally occurring glasses and glass waste forms, as their compositions and thermal histories are very different; however, natural glasses may serve as standards of comparison for laboratory experiments designed to evaluate the long-term stability of synthetic glass waste forms.

A similar report evaluating the long-term stability of natural analogues to crystalline waste forms is in progress.

SECTION 3 - ALTERNATIVE WASTE FIXATION PROCESSES

The goal of this task is to develop alternative waste fixation procedures that will serve as viable backup processes. Cost and safety factors of the alternative processes and products are to be compared to those of the current reference process and product--silicate glass castings in large metal canisters. These alternative processes are being developed on the laboratory scale. In the concept currently emphasized the waste is formed into small granules or pellets that are coated with nonradioactive, inert materials to provide containment and leach resistance. The coated waste shapes are then incorporated into a metal matrix that provides impact resistance and increased thermal conductivity.

MULTIBARRIER WASTE FORM DEVELOPMENT - J. M. Rusin

Four 1-liter stainless steel canisters have been produced to demonstrate the multibarrier concept. The concepts, in order of increasing technological complexity, were:

- simulated waste-glass marbles encapsulated in a Pb-10Sn vacuum-cast matrix
- uncoated sintered supercalcine pellets encapsulated in an Al-12Si vacuum-cast matrix
- glass-coated sintered supercalcine pellets encapsulated in an Al-12Si vacuum-cast matrix
- chemical vapor deposition (CVD)-coated supercalcine [coated with a Pyrolytic Carbon (PyC)/aluminum-oxide combination] encapsulated in a copper gravity-sintered matrix.

Characterization of these multibarrier waste forms is discussed in Part II of the "Multibarrier Waste Forms" report (Rusin, et al., 1979).

It is recommended that the multibarrier concept of glass marbles encapsulated in a vacuum-cast lead alloy be pursued for further development. This concept provides increased inertness with a minimum increase in technological complexity. The performance of glass as an acceptable waste form has been documented (Mendel, et al., 1977).

Future development of the marble multibarrier concept would only require demonstration of marble manufacture and matrix encapsulation. If it were desirable to develop a crystalline multibarrier waste form, uncoated sintered supercalcine pellets would offer increased inertness at a much lower level of technological complexity than would glaze- or CVD-coated supercalcines. Chemical vapor deposition coating of supercalcine should be pursued only if a very high level of inertness is required.

Although the formulation and production of sintered supercalcine (an assemblage of crystalline solid solution phases) has been demonstrated on a laboratory scale, further development is required to establish the performance of crystalline waste forms. For example, phase formulation models have been successfully demonstrated for a low-sodium reference waste (PW-7) at waste loading levels of between 60% and 80%. Further development is needed to demonstrate the applicability of the supercalcine concept to the reference high-sodium- and high-phosphate-containing wastes and to thorium fuel cycle wastes, which contain the additional elements aluminum, potassium, fluorine, and thorium. The overall thermal stability of supercalcines must be demonstrated (especially for the scheelite phase) along with a determination of the degree of non-crystallinity in supercalcines. Radiation stability of supercalcines also needs to be determined. It is for these reasons that glass marbles are preferred over supercalcines at this time.

The following recommendations are made from the contents of the report, Multibarrier Waste Forms Part I: Development (Rusin, et al., 1978):

- selection of glass marbles encapsulated in a vacuum-cast lead alloy as the multibarrier concept for further development
- selection of uncoated sintered supercalcine pellets encapsulated in a vacuum-cast aluminum alloy for further development if a crystalline multibarrier concept is desired
- demonstration of full-scale production of glass marbles by a marble casting process integrated with the PNL tilt-drain continuous ceramic melter
- demonstration of full-scale encapsulation by vacuum casting for glass marbles in a lead alloy and uncoated supercalcine phases
- investigation of lower-cost alloys for vacuum casting
- development of improved bonding in gravity-sintered matrices
- discontinuation of the glass coating of supercalcine
- discontinuation of the development of CVD coatings unless maximum inertness is required
- use of the disc pelletizer without scaleup, since the existing 16-in. unit has sufficient capacity for a large PNL (∿50 liter/hr) spray calciner.

SINTERED AND HOT-PRESSED CERAMICS - J. M. Lukacs, L. R. Bunnell and W. J. Gray

Previous experience with spray-calcined powders showed them to be x-ray amorphous. Examination of as-produced PW-9 showed the presence of sodium molybdate (Na_2MO). This phase remained even after sintering at temperatures above 800°C, where an unidentified crystalline phase was detected.

Initial sintering trials have been completed with several frit, oxide, and mineral additions. By using weight loss and shrinkage data, optimum sintering temperatures were identified for each calcine mixture to produce the densest sample without significant deformation or melting. This information is being used to fabricate sintered ceramic specimens for volatility, impact resistance, and leach resistance characterization tests.

Selected compositions will be hot-pressed and hot-isostatically-pressed (HIP) to evaluate the impact that processing has upon waste storage criteria. Samples of hot-pressed PW-9 calcine have been produced. Arrangements with BCL have been made to HIP several compositions this year.

THE PENNSYLVANIA STATE UNIVERSITY SUPERCALCINE INVESTIGATIONS -

G. J. McCarthy, Program Leader

Formulations for High-Sodium Supercalcine

During the last two months current formulations for high-sodium supercalcines have been optimized. The basic phase formation model is listed in Table 6. The crystallization and

TABLE 6. Phase Formation Model for High-Sodium Supercalcines

Waste Ion	Supercalcine Phase
Na,Mo,Sr,Ba	$(Ca,Sr,Ba)\ [NaAlSiO_4]_6MoO_4\ [So_{ss}]$
Cs,Rb	$(Cs,Rb)AlSi_2O_6\ [P]$
RE(La,Pr,Nd,Sm,Eu,Gd,Y), Sr, PO_4	$(Ca,Sr)_2RE_8[SiO_4]_6O_2\ [A_{ss}]$ $REPO_4\ [M_{ss}]$
U,Ce,Zr	$(U,Ce...)O_{2+x}[F_{ss}]$ $(Zr,Ce,U...)O_{2+x}[T_{ss}]$
Fe,Ni,Cr	$(Fe_2O_3)_{ss}$ and $(Fe,Ni)(FE,Cr)_2O_4\ [SP_{ss}]$
Pd,Rh,Ru	As metals
Te,Cd,Ag	As minor solid solution substitutions in other phases

effective compatibility of the major phases [A_{ss}, F_{ss}, T_{ss}, P, $(Fe_2O_3)_{ss}$] have been confirmed by x-ray characterization of laboratory-scale simulations. Three formulations (SPC-5A,B,C) based on this phase formation model have been developed.

Thermal Stability of $(Ca,Sr,Ba)MoO_4$ [S_{ss}] Phases

Molybdenum oxide(s) constitute the major component(s) of the species volatilized from SPC-2 and SPC-4 during the prolonged firings (12 to 36 hr) at high temperatures (1200° to 1400°C). A study was initiated to determine whether the S_{ss} alone was responsible for the MoO_x losses.

We have completed the literature survey for previous work in this system. No indication has been found of any work having been performed on the $SrMoO_4$-$BaMoO_4$-$CaMoO_4$ ternary system. No literature describing work on the $SrMoO_4$-$BaMoO_4$ and $CaMoO_4$-$BaMoO_4$ binaries has been located. Matveeve and Maier (1967) found that $CaMoO_4$ and $SrMoO_4$ are thermodynamically stable at their melting temperatures and that they do not react with MgO, Al_2O_3, $MgAl_3O_4$, and ZrO_2 (stabilized by 10% CaO) refractories. In summary, the literature indicates very refractory properties for alkaline earth molybdates, even above their melting points.

Crystalline phase-pure end members ($CaMoO_4$, $SrMoO_4$, and $BaMoO_4$) and four typical S_{ss} compositions were synthesized and then characterized by TGA. Each of the end members had very low weight losses--in no case more than 0.4 wt% in 24 hr at 1300°C. The least refractory of the three was $CaMoO_4$. No evidence of dissociation of any of the pure molybdates was observed. This temperature is higher than proposed SPC processing temperatures by about 100°C, so we can confirm that the pure end member $AEMoO_4$ scheelites are quite refractory under relevant conditions.

With the completion of TGA studies on S_{ss} phases, it has become evident that the small MoO_x volatilization losses in supercalcine-ceramics heated at high temperatures for long durations cannot be attributed to poor thermal stability of the S_{ss} phase itself.

There are two other possibilities for these losses. First, the S_{ss} phase could be marginally incompatible with another supercalcine phase so that it slowly reacts with it and releases MoO_x. Second, the level of alkaline earth (Ca,Sr) additives in the supercalcine may be inadequate to fix all Mo as $AEMoO_4$ because other phases (e.g., A_{ss}) incorporate more AE than is implied by their nominal stoichiometries. Both possibilities are being explored.

Conventional Hot Pressing of SPC-4

Our brief studies in this area are complete and a topical report has been prepared. The report describes the role of the spray supercalcine powder characteristics and hot-pressing temperature on densification/consolidation, microstructure, and crystallinity. It features characterization of the as-received and modified supercalcine powders and of the supercalcine-ceramic product by a computer-controlled SEM.

CHEMICAL VAPOR DEPOSITED COATINGS - M. F. Browning and R. W. Kidd, Battelle-Columbus Laboratories

The experimental effort during this report period has been directed toward the following areas:

- preparation of Al_2O_3-coated SPC-4 (2 to 3 mm) for evaluation at PNL
- preparation of duplex-coated (Al_2O_3 over PyC) PyC-2 (1 to 2 mm)
- continued development of a drum coating technique for applying Al_2O_3 coatings over PyC-coated SPC-4 in the 5- to 9-mm size range.

In the current program, roughly 1450 g of 2- to 3-mm-dia Al_2O_3-coated SPC-4 particles were produced in seven runs. Thickness of the Al_2O_3 coating varied from 20 to 50 μm, depending upon run conditions. The coating rates were typically 9 μm/hr. The materials prepared in all but one run appeared to have smooth and dense coatings of good integrity. The coating on the product from this run appeared to have a rougher surface, presumably because of insufficient agitation near the end of the run.

Roughly 330 g of duplex-coated (Al_2O_3 over PyC) SPC-2, 1- to 3-mm particles were produced in two runs. The PyC and Al_2O_3 coating thicknesses were 44 μm and 55 μm, respectively. The Al_2O_3 coating rate was ∿5 μm/hr. Oxidation of a typical sample at 750°C in air for 24 hr suggests that the Al_2O_3 coating was protective in that a weight loss of only 0.23 wt% was measured. Complete loss of the PyC layer would have given a weight loss of ∿3.2 wt%. The coatings applied in these runs appeared to be of comparable quality to those previously produced for the one-liter demonstration.

Larger supercalcine particles (5 to 9 mm) are more efficiently produced in the disc pelletizers and are easier to handle. In addition, since the coating occupies less of the total waste form volume for larger particles, the waste loading of the waste product is increased. Thus, a major objective of the CVD program is to demonstrate that a protective Al_2O_3/PyC coating can be applied to relatively large-sized (5- to 9-mm) SPC-4 material using a drum-coating technique, which is considered to be more practical than a fluidized bed or vibrating bed for coating the larger-size substrates. This is continuation of work initiated in the previous program. Since in this earlier work an apparently satisfactory procedure for applying PyC coatings to larger particles was developed using a fluidized-bed technique, the initial effort during this time period was to apply only Al_2O_3 coatings in a drum coater.

Only a limited supply of relatively large-sized SPC-4 material was on hand for use: 200 g of 2.6- to 4.6-mm particles and 300 g of 5- to 9-mm particles. Since the larger size was ultimately of more interest, the smaller material was used during the coating parameter definition phase.

Progress has been made in defining the coating procedures that appear attractive for obtaining a duplex coating of Al_2O_3 over PyC on the large-size substrate; however, the objective was not fully achieved. The major problem in obtaining a duplex coating seems to rest in producing a PyC coating that is able to survive the Al_2O_3 overcoating. PyC coatings have typically either flaked off when subjected to any mechanical abuse, or have been lost by oxidation during the Al_2O_3 overcoating.

CARBON LEACH TESTING - W. J. Gray

Carbon is expected to have a very low leach rate and, therefore, is attractive as one of the barriers of a multibarrier waste form. Tests to determine the leach rate of carbon are in progress. Oxidation, rather than leaching, is probably a more accurate description of the mechanism of carbon removal in aqueous systems. Nevertheless, the removal can be described in terms of g/cm^2-day and compared with the leach rates of other materials.

The experimental approach has been to stir powdered (-325 mesh) graphite and water at $\sim 95^{\circ}C$ in a sealed container. Water is extracted from the container through a filter; carbon in the water is oxidized to CO_2, and the CO_2 content is determined using infrared absorption spectroscopy. The detection limit for the carbon analyzer is about 1 ppm.

Considerable difficulty has been experienced so far in obtaining blank runs with essentially no carbon. Only one carbon leach test has been made in which the results were considered to be valid. In that test, less than 1 ppm carbon was detected after a 90-hr test at $\sim 95^{\circ}C$ in distilled water. This is equivalent to a leach rate of $<1.4 \times 10^{-11}$ g/cm^2, assuming that all carbon dissolved from the graphite remained in the water. Dissolved carbon seems likely to be in the form of CO_2 or CO. Carbon dioxide would be about equally distributed between the liquid and gas phases, but only about 2% of the CO would remain in the water. If all the dissolved carbon was CO, the calculated leach rate should be multiplied by about 50. This is still a very low rate.

Some ^{14}C-labeled material has been ordered that will lower the leach rate detection limit by a factor of between 100 and 1000. Using ^{14}C also eliminates the problem of trying to obtain blank runs with essentially no carbon. Analyses will be made of both the liquid and gas phases. Tests are planned to determine leach rate dependence upon time, temperature, pH, salt or other mineral content of water, and types of carbon. Finally, the effect radiation has upon leach rates will be investigated.

REFERENCES

Matveeve, E. V. and A. A. Maier. 1967. Tr. Mosk. Khim. Tekhnol. Inst., 55, 172.

McElroy, J.L., J.E. Mendel, W.F. Bonner and M.H. Henry. 1979. Quarterly Progress Report - Research and Development Activities - High-Level Waste Immobilization Program: January Through March 1978. PNL-2999-1. Pacific Northwest Laboratory, Richland, WA 99352

Mendel, J. E. et al. 1977. Annual Report on the Characteristics of High-Level Waste Glasses. BNWL-2252, Pacific Northwest Laboratory, Richland, WA 99352.

Rusin, J. M. et al. 1978. Multibarrier Waste Forms Part I: Development. PNL-2668-1. Pacific Northwest Laboratory, Richland, WA 99352.

Rusin, J. M. et al. 1979. Multibarrier Waste Forms Part II: Characterization and Evaluation. PNL-2668-2. Pacific Northwest Laboratory, Richland, WA 99352.

Smith, T. H. and W. A. Ross. 1975. Impact Testing of Vitreous Simulated High-Level Waste in Canisters. BNWL-1903. Pacific Northwest Laboratory, Richland, WA 99352

PNL-2999-3

HLWIP QUARTERLY REPORT
JULY THROUGH SEPTEMBER 1978

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QUARTERLY PROGRESS REPORT
RESEARCH AND DEVELOPMENT ACTIVITIES
HIGH-LEVEL WASTE IMMOBILIZATION PROGRAM:
JULY THROUGH SEPTEMBER 1978

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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 July through September of 1978:

- A power outage interrupted operation of the calcine-fed ceramic melter (CFCM) for 4.4 hr and the liquid-fed ceramic melter (LFCM) for 2.5 hours. Operation of both melters was resumed without auxiliary heating. The severe reboil that occurred subsequently in the LFCM may have been due to the gas dissolved in the molten glass during the electrical outage.
- A generic waste glass properties study has been started. The full study will evaluate the influence of 26 oxide components, including glass formers, modifiers and intermediates on waste glass properties. The method will be tested first on a smaller field involving 10 oxide components and narrowed composition range.
- Curium was found to accumulate equally in two devitrification phases in a waste glass--$Gd_2Ti_2O_7$ and a complex phosphate rich in gadolinium and calcium. The latter phase is undergoing a crystalline-to-amorphous transformation; the former is apparently unaffected by radiation.
- Development of supercalcine for evaluations of Thorex waste compositions has started. Fluoride can be contained in an apatite phase, $Ca_4Nd_6SiO_46F_2$, prepared at 900^0 to 1000^0C. The phase decomposes slowly if held at these temperatures, however.

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 and -2999-2.

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JULY THROUGH SEPTEMBER 1978

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 FIXATION PROCESS DEVELOPMENT

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

CERAMIC MELTERS - C. C. Chapman, J. L. Buelt, R. D. Dierks

The calcine-fed ceramic melter (CFCM) was tested using the internal air-cooled passages in the electrodes. Control of the melter was stable even with large differences in cooling rates. The electrodes could be cooled some 200° to 250°C below the temperature of the bulk glass without difficulty. The use of this electrode cooling may allow higher-temperature glass compositions to be produced in the lower-temperature electrode material, Inconel-690.

In the first week of July, power to the Engineering Development Laboratory was off for the three phases about 5-1/2 hr and the CFCM was without power for that time. After the return of normal power the unit was able to recover without auxiliary assistance. The liquid-fed ceramic melter (LFCM) has a single-phase power supply and is on a different phase of the three-phase supply for the Engineering Development Laboratory. Therefore, it was without power for only 2-1/2 hours. It also recovered without requiring auxiliary heating. These results, although not planned, are an indication that some freedom exists for simple recovery of operation of a continuous ceramic melter, should power be lost.

As would be expected, the glass temperature within the two continuous melters dropped rapidly. Temperatures as low as 600° to 700°C were present at the top of each unit. However, the core of the body or bulk of glass remained sufficiently conductive to allow current flow upon return of power.

An aqueous feeding test was initiated in the LFCM one week after the power outage. A maximum process rate of 145 ℓ/hr of aqueous feed was being maintained. However, the test was interrupted after 8 hr of operation when the glass re-boiled and bubbled glass foam through the sintered crust. A large quantity of material (molten glass foam) came into contact with the aqueous hold-up and caused rapid heat exchange and evaporation of the hold-up. The rapid flashing of feed to steam resulted in the flooding and pressurization of the off-gas system. The degree of re-boil was larger than had been experienced in previous experiments. The reason for the increased re-boil effect is believed to be the power outage and the large decrease in temperature that took place. Gas solubility is higher at lower temperatures. Evaluation of dissolved gas can cause foaming (re-boil) when the temperature is increased. Some compositions are more vulnerable to the re-boil phenomenon when re-heated than are others. Because the glass contained in the LFCM appeared to be susceptible to the re-boil phenomenon, a flush-out run was made so that a composition less susceptible to foaming could be used. During the flush-out run, higher and higher production rates were achieved before re-boil would again pump foam on top of pre-melted frits. This flush-out experiment strongly suggested that re-boil would not occur until some previously achieved maximum temperature had been exceeded or until a region that is normally cold finally exceeds some specified temperature limit. This unusual behavior of glass suggests that a greater emphasis needs to be placed upon evaluating its consequences.

An experimental method was developed to determine the amount of volatile materials that are released from the continuous melter during idling conditions. The amount and composition of constituents coming out of the melter during non-production modes, as shown in Table 1, will be of interest to operational plant staffs. The experiment arrangement shown for the LFCM is given in Figure 1. During idling conditions the normal off-gas line is valved out and the arrangement shown in Figure 1 is placed on a flange and used as the only out-gassing line. The water-cooled stainless steel Mister Mesh® is used to collect the volatile material that escapes from the LFCM. The temperature of the glass surface in the LFCM was altered by changing the power in the melter. Two surface temperatures were tested: 800°C and 675°C. A total of three days' collection was used in these experiments. The most volatile species was sodium.

EFFLUENT CONTROL - M. S. Hanson, C. A. Knox and W. E. Sande

A laboratory-scale spray calciner and in-can melter, designed primarily for effluent studies, has been constructed and installed in EDL-102. The calciner/melter system is designed for fully remote operation. Preliminary testing of the calciner at low feed rates (less than 1 ℓ/hr) has proven its operability. The feed for the test was TW-3, a fluoride-containing simulated Thorex waste. A small amount of calcine was produced for glass formulation.

Design of remote-feed and off-gas systems is nearing completion.

Simulated Thorex waste TW-3 was fed to the pilot-scale spray calciner/in-can melter with the primary intent of studying corrosion in the off-gas system. Coupons placed throughout the off-gas system showed negligible weight loss and optical examination revealed no unusual effects.

TABLE 1. Volatility of Glass Components During Idling (SRP Glass Composition)

Oxide	Glass Composition, wt%	Volatility Rate for Hot Glass Surface, g/day	Volatility Rate for Cool Glass Surface, g/day
SiO_2	39.4	0.12	Neg'l
Na_2O	13.9	5.3	<0.024
TiO_2	7.5	Neg'l	Neg'l
B_2O_3	7.5	0.20	<0.021
CaO	4.6	Neg'l	Neg'l
Li_2O	3.0	0.14	Neg'l
Fe_2O_3	8.4	Neg'l	Neg'l
Al_2O_3	12.3	Neg'l	Neg'l
MnO_2	2.8	Neg'l	Neg'l
NiO	0.6	Neg'l	Neg'l

®Mister Mesh is a product of A.C.S. Industries, 71 Villanova St., Woonsocket, RI 02895

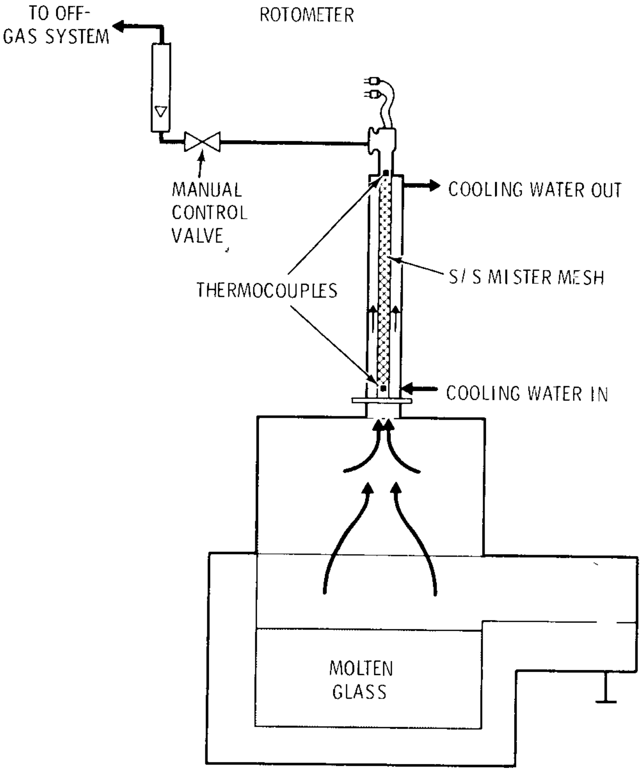

FIGURE 1. Particulate Collector

IN-CAN MELTING DEVELOPMENT - H. T. Blair

Five in-can melting (ICM) tests were made in the non-radioactive process demonstration facility using simulated waste compositions during the last reporting period. One of the tests was made in the full-scale in-can melter using a 28-in.-dia can to determine the maximum melting rate that can be sustained in this size of melter. The other four runs were made in the pilot-scale melter: two were performed to evaluate the operating factors to be used in the Nuclear Waste Vitrification Project, one was made to evaluate the melting behavior of a new SRP frit composition, and the final test was made to demonstrate vitrification of an alternate fuel cycle waste composition using the in-can melting process.

A 117-kg/hr maximum melting rate was sustained for nearly 6 hr during the test in the full-scale ICM with the 28-in.-dia can. The average melting rate for the overall running time of 15 hr was 108 kg/hr. These rates are presented in Figure 2 along with previous results for comparison. The reason the rates achieved in the 28-in.-dia can are so much better than those demonstrated in the 14-in. is because the heat transfer plate assembly design used in the 24-in. can was not as efficient as was the design used in both the 20-in.- and 28-in.-dia cans.

The run was terminated before the can was completely filled because the connecting section became plugged when a bag of wet frit was fed into the system. As soon as the plugged condition was detected, the calciner and melter were shut down so that the cause could be determined. The wet frit had caused moisture to collect in the diverter valve and a plug of

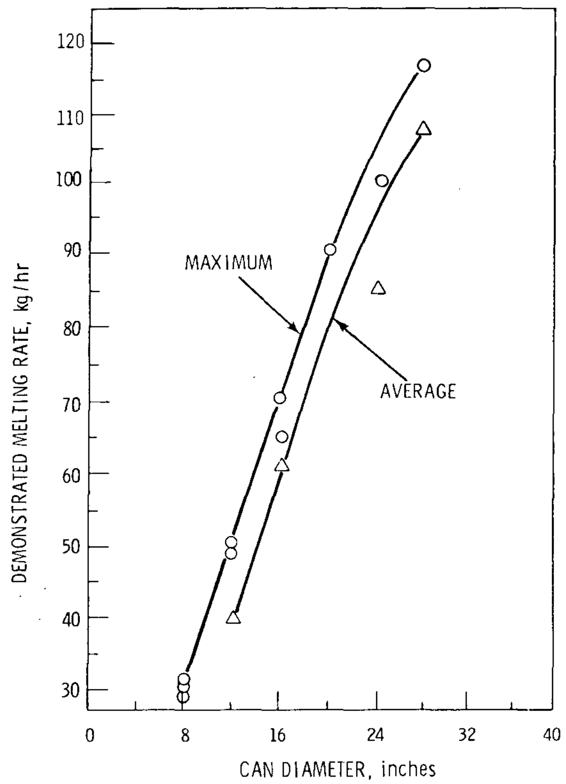

FIGURE 2. In-Can Melting Rate as a Function of Can Diameter

calcine formed there. Activation of the diverter dislodged the plug, which moved down the sloping leg of the connecting section and became lodged against the sheath around the cone valve stem. The plug was very friable and could have been easily broken up if the sheath were movable.

The two pilot-scale in-can melting runs performed in support of the Nuclear Waste Vitrification Project (NWVP) were made using a retort and the insulating collars designed for use in the hot-cell furnace. The melter was coupled directly to the spray calciner, which was producing calcine at the rate proposed for the cell operation. Frit was proportionally fed into the system by adding weighed quantities every 10 minutes through the flapper-gate-type airlock.

The furnace was maintained at 1000^{0}C during the processing of the first can. The most significant result of the first test in the series from an operations viewpoint was that as the melt level approached to within a foot of the top of the furnace hot zone, the batch would no longer melt as fast as it was entering the melter. The batch charging rate at that time was only 2.4 kg/hr. Charging of the ICM was terminated when a cold cap had formed which was rising above the heated part of the can. Four to five hours were required to completely melt this cold cap down. The low melting rate is due to the low operating temperature (1000^{0}C) and the large heat losses at the top of the can caused by the retort and the can extending through the insulation at the top of the furnace, where the temperature was 900^{0}C. We hope that we will be able to compensate for some of this heat loss in the hot cell, as it is a multizone furnace and the top zone may draw more power without causing overheating lower in the furnace.

During the second run in the series the furnace temperature was increased to 1050°C, and 1.5 wt% powdered silicon metal was added to the batch by blending it with the frit. All other operating factors were the same as during the first test. To assure proper proportioning of frit to calcine, the frit was added to the melter by weighing out 533-g quantities and dumping them through the airlock every 10 minutes. The result was poor frit and calcine blending, which resulted in poor melting. Toward the end of the run the frit was added using a continuously operating screw feeder. The melting improved considerably.

The run for SRP was made in the pilot-scale melter using an 8-in.-dia can containing an 8-radial-fin assembly. The batch for the run was a blend of spray-dried, simulated SRP composite waste with SRP Frit 411. A melting rate of 15.2 kg/hr was sustained for 2 hours. The charging rate was then increased to 17.2 kg/hr. Within an hour the batch had to be shut off because a cold cap had formed. One half-hour was required to melt the cap. No foaming was observed, although there was significant gas evolution during the melting. Batch was then charged for a period of 1 hr at a rate of 13.5 kg/hr. An accumulation of unmelted batch had reached the top of the fin assembly by that time, and the test was terminated. The cold cap melted rapidly and the melt appeared very fluid as bubbles burst at its surface. Although this batch composition did not foam as it melted, a melting rate no greater than 15 kg/hr could be sustained under ICM operating conditions, whereas 30 kg/hr is usually achieved using simulated commercial compositions and frits developed at PNL.

The last test performed during the reporting period was made to evaluate the melting behavior and product of vitrifying alternate fuel cycle waste. The excessive output of the frit feeder resulted in a higher than desired frit charging rate to the ICM, and we were unable to determine the optimum melting rate at the desired frit-to-calcine ratio. Several interesting things were observed during the melting, however. There was a dense fume in the melter during melting and blue-white flames were frequently seen at the melt surface. The product is a homogeneous glass except for some second phase material at the very bottom of the can. Also, no slag layer was found on the top of the product.

CANISTER DEVELOPMENT PROGRAM - S. C. Slate

Full-Scale Canisters Filled by Continuous Melting - S. C. Slate and C. R. Hymas

During this period, six canisters were filled with glass from the spray calciner/calcine-fed ceramic melter system during ten days of continuous operation. An SRP-composition glass was used. All of the canisters, like the one in Figure 3, were made from A-53 carbon steel, and were 24 in. in dia with a 0.250-in. wall. The canisters were placed in an insulated enclosure during filling so that the incoming glass would remain hot enough to flow and prevent void formation. We removed the side from one canister and it appeared that insulating the canister did significantly reduce the layering and voids that have been observed in noninsulated canisters.

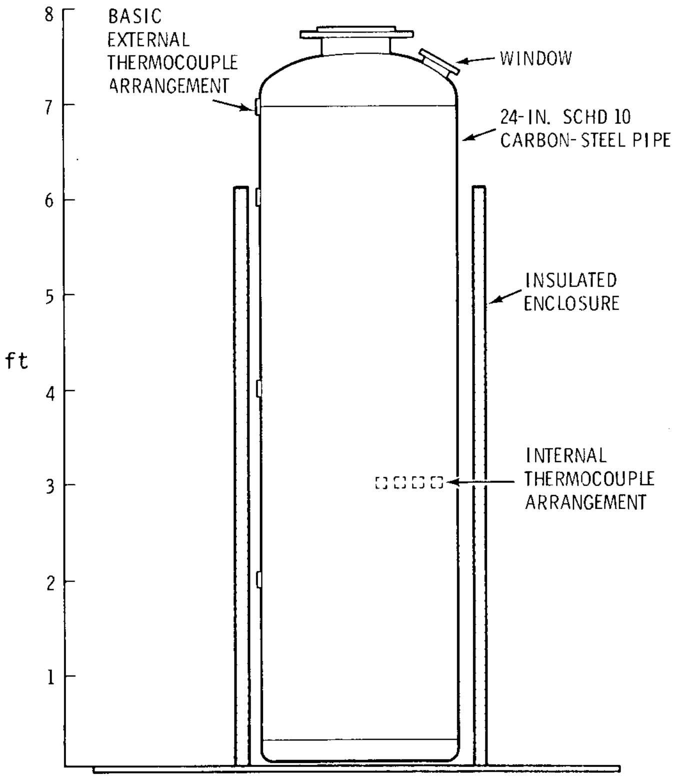

FIGURE 3. Canister in Insulated Enclosure

A summary of the type of data that was gathered on each of the canisters is shown in Table 2. During the filling period, which averaged about 36 hr, external and internal temperatures were monitored. During filling, the maximum wall temperature ranged between 520°C and 590°C. After the canister was filled it was connected to another recorder to obtain cooldown temperatures. Figure 4 shows the time varying temperature gradient from the centerline to the wall for one of the canisters. (The time of 0 hours was arbitrarily selected and is not when the canister was removed from the enclosure.) This data is important in understanding cracking and compositional differences that have been observed in this glass.

We measured changes in the canister diameter using a tape and a micrometer. Some canisters showed a slight increase, while others showed a slight decrease in diameter. The average change was usually less than 0.010 in. and was frequently less than 0.005 inches. We can conclude from this data that the amount of canister deformation occurring during canister filling and cooldown insignificant.

TABLE 2. Canister Data Summary

Order	Canister Number	Canister Wt., kg	Filled Wt., kg	Filling Time, hr	Number of External T/C's	Special T/C Arrangement	Number of Internal T/C's	Maximum Wall Temp., ^{o}C	Average Cooling Rate, ^{o}C/h$^{(a)}$	Average Change in Dia	Wall Removed (yes/no)
1	71	272	2264	33.5	4	None	0	470	NA	NA	no
2	72	281	1554	47.0	9	4 ea.@ 36-in. level. Equal-spaced.	4	525	14	NA	no
3	73	277	1750	31.7	6	3 ea. 1.5-in. centers. Vertical spacing.	0	595	45	-0.008	no
4	74	271	1749	35.7	6	2 ea. 90^{o} apart @ 1-f level.	0	520	30	-0.003	no
5	75	276	1740	33.5	13	4 ea. @ 36-in. level. Eq.-Sp. 2 ea. Inside & Out @ 56 in.	5	550	14	+0.005	yes
6	78	274	1739	32.7	5	None	4	590	13	+0.003	no

(a) This is the cooling rate to 250^{o}C; the rate from 250^{o} to 100^{o}C averaged ∿9^{o}C for all canisters.

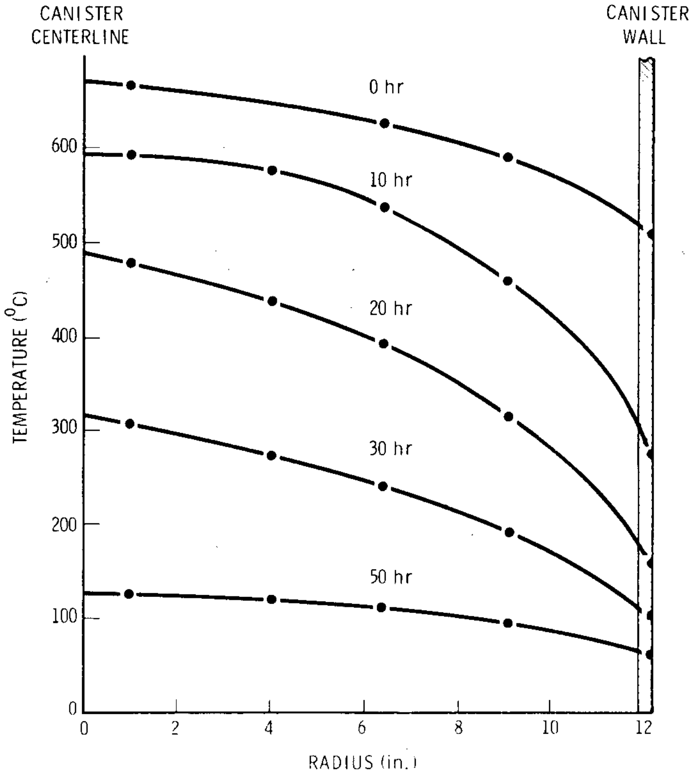

FIGURE 4. Internal Glass Temperatures in a Canister as a Function of Time

High-Temperature Strain Monitoring of a Continuous Melting Canister - R. J. Kurtz and S. C. Slate

In the design of waste canisters it is helpful to know the strain levels in a canister that result from the mechanical and thermal loadings that occur during filling. Empirical data on the strain levels are also useful in verifying computer codes that are used to model canister behavior. Strain measurements on large structures are often quite complex, but tend to produce data that indicate the true structural response to given mechanical and thermal loading. With this in mind, high-temperature strain measurements were made on a prototype canister during filling of that canister with simulated waste glass.

The strain measurements were made with high-temperature (to 550°C) strain gauges that were spot welded to the exterior wall of a mild steel canister 24 in. in dia by 10 ft high, as shown in Figure 5. Chromel-Alumel thermocouples were also attached to the canister in the vicinity of each group of strain gauges to enable temperature corrections to the data. Data from the nine strain gauges was taken every ten minutes throughout the duration of the test. For each strain gauge grouping, appropriate temperature readings were made between each strain gauge measurement.

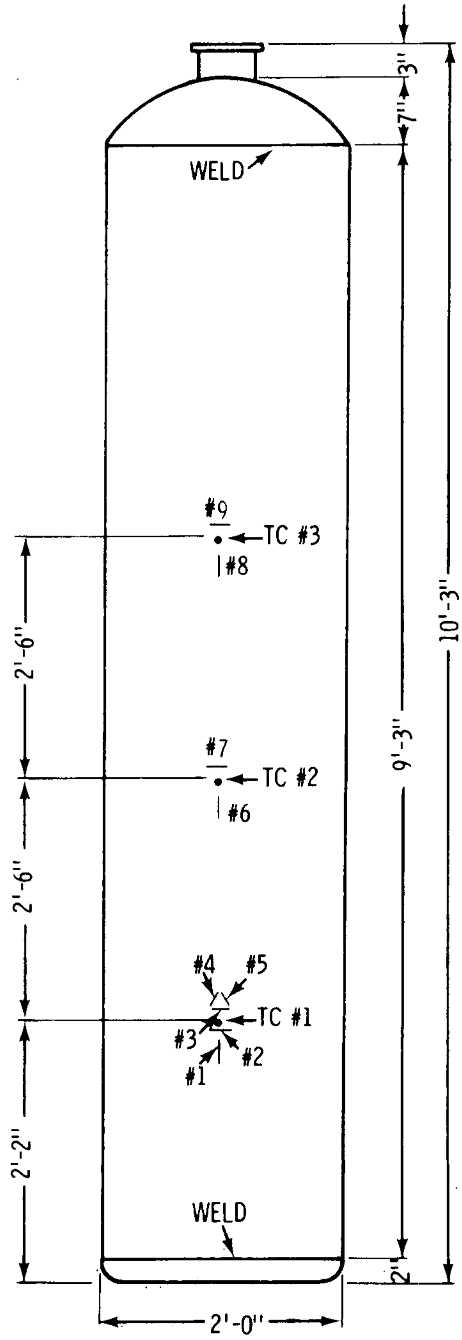

FIGURE 5. Strain Gauge and Thermocouple Locations on the Waste Canister(a)

(a) Note that all gauges were located 180° opposite the longitudinal seam weld.

The sample plot of strain gauge data that is shown in Figure 6 tends to parallel the temperature versus the time history that was observed, and which is plotted in Figure 7. Each strain gauge group reached its peak strain reading when the corresponding thermocouple reached maximum temperature. The strain data also indicates that the canister yielded very early in the pouring. After filling for about 90 min, the bottom set of strain gauges exceeded the yield strain. Furthermore, after reaching the peak strain, a gradual strain recovery was observed that generally coincided with the temperature decay caused by cooldown. The explanation of these results is not clear at this time. The reason for canister yielding so early in the pouring operation cannot be attributed to the mechanical loading of the canister from the static head of the glass, since only about 0.75 ft of glass had been poured into the canister. Some visual evidence was obtained suggesting that severe thermal gradients may have contributed significantly to the stressing of the canister. The influence of these large thermal gradients is not readily explained, since the gauges were supposedly temperature-compensated. Perhaps using the mean thermal expansion coefficient over the temperature range 25°C to 550°C was responsible for this effect. If the data are presumed to represent the

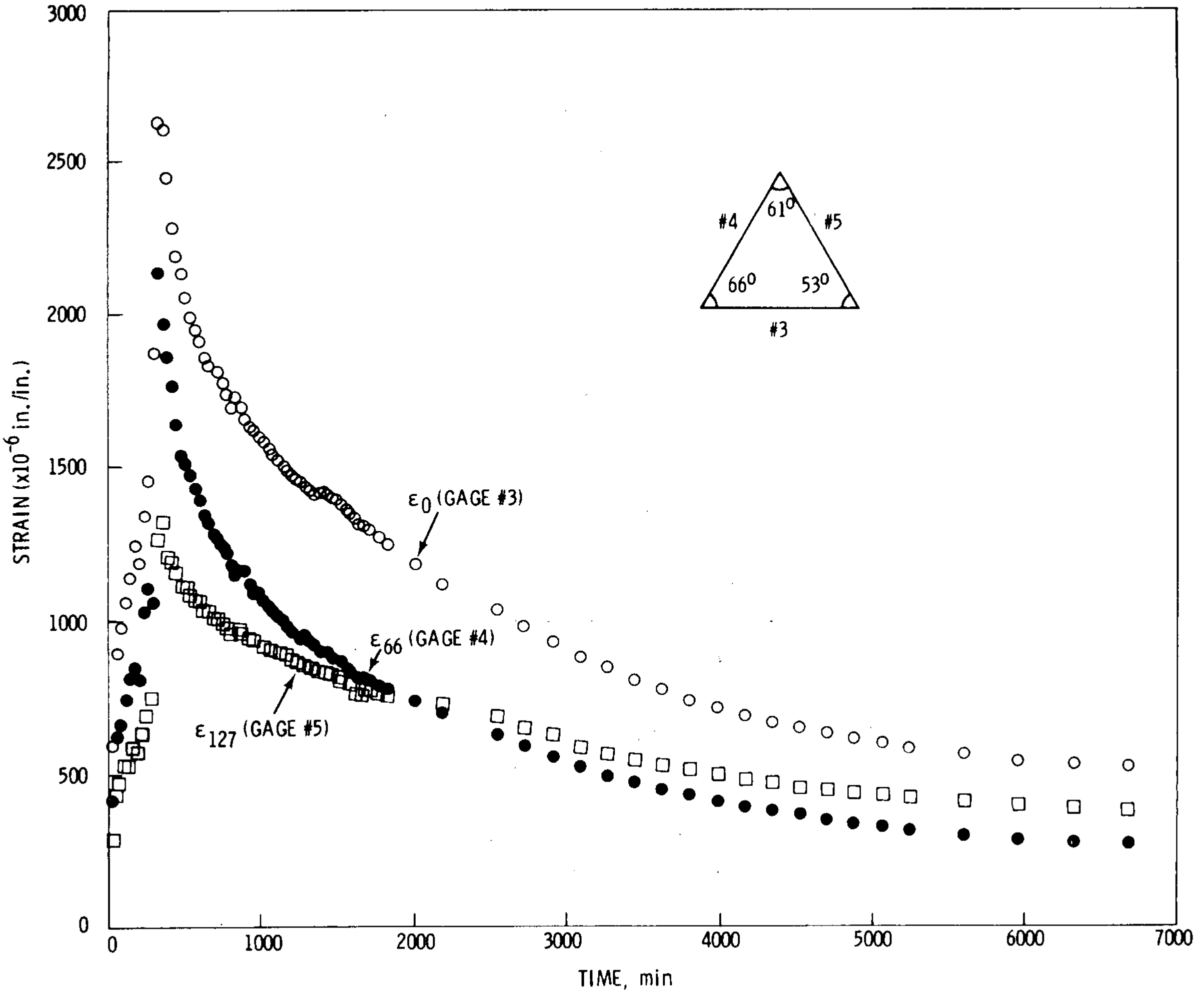

FIGURE 6. Corrected Strain Versus Time Readings for Strain Gauge Numbers 3, 4, and 5

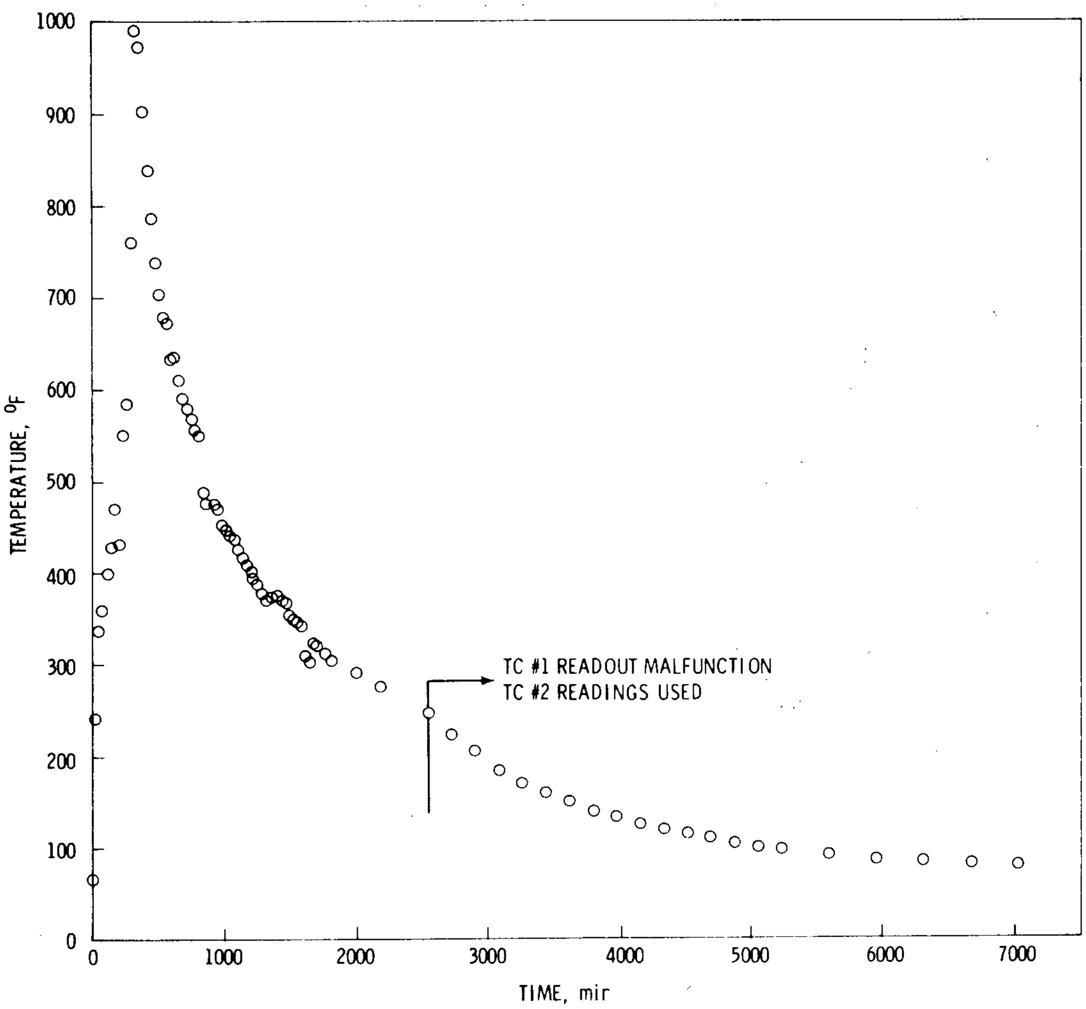

FIGURE 7. Temperature Versus Time History for Thermocouple Number 1

true behavior of the canister, then a large amount of the strain relaxation or reverse straining occurred during cooldown. The driving force for this strain relaxation is not clear at this time. It may have been due to relaxation of applied residual stresses. It is highly probable that the canister was not stress-relieved prior to pouring. Results also indicated that the principal strain axes were rotated counter-clockwise about 22°C from the axis of canister revolution, as shown in Figure 8. This result was not considered unusual, due to the possibility of non-uniform dimensional distortions in the large canister structure.

All the strain gauges were reading a finite positive value once the canister temperature returned to ambient conditions. These readings can be considered accurate, since no temperature effects need to be considered. These results also indicate that the canister did yield at some point in the loading history and that all the strain was not recoverable. Post-test micrometer and Pi-tape measurements verified that in fact the canister had yielded slightly.

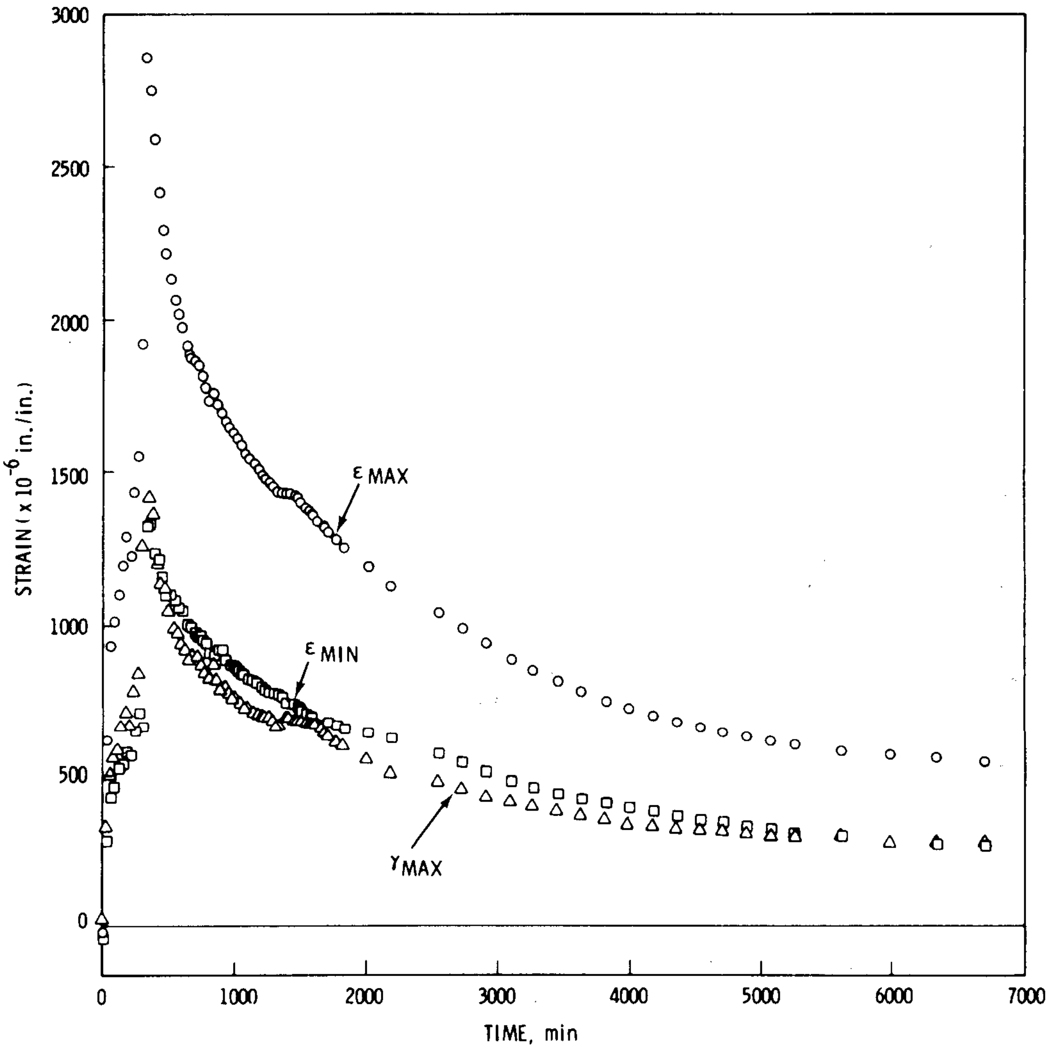

FIGURE 8. Calculated Principal Strains Versus Time from Strain Gauge Numbers 3, 4 and 5

SECTION 2 - WASTE FORM CHARACTERIZATION

The purpose of waste form characterization is to measure the properties of candidate solidified products and containers (solidified waste and canister) as functions of composition, processing parameters, and storage conditions. The measurements are used to: 1) ensure operability of the vitrification processes and 2) provide data for safety analyses of high-level waste management. The ultimate goal of waste characterization 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 a final disposal site, we may be fully confident that their behavior is understood and that any changes or interactions with their environments are wholly predictable.

GENERIC WASTE GLASS PROPERTIES STUDY - L. A. Chick

Planning was completed this quarter for a new waste glass formulation study. The objective of the generic study is to develop the ability to predict the important properties of glasses within a wide range of compositions centered around those of waste glasses from several national sites.

Analysis of 35 presently developed waste glasses showed that 56 elements occurred as components. Elimination of those elements never occurring at more than 0.1 mole%, and combination of elements expected to act similarly in glasses reduced the number of components to 30. Fluorine, chlorine, sulphur, and carbon were partitioned off for a separate study because these present special problems for control of experimental composition due to their high volatility from melts. Table 3 lists the remaining 26 elements (as oxides) which comprise the independent variables of the study. Seven groups of similarly acting oxides are included, as shown in Table 4. Each group will be represented in the study by the footnoted member. The minimum and maximum allowed concentrations (mole%) of the study components are listed as "-" and "+" levels.

Experimental designs utilizing test compositions with most components at either their minimum or maximum values are being developed. Sets of test compositions composed of these extreme vertices and other, more centralized compositions, are best for the purpose of fitting mathematical approximation models to the response of measured properties.

The following is a list of properties that will be determined for generic study:

- viscosity at 1000°C and 1200°C
- resistivity at 1000°C and 1200°C
- leachability: Soxhlet and pH4
- devitrification: percent crystals on as-melted and on slow-cooled
- volatility: total wt% loss at 1000°C and 1200°C after 3 hr
- quality: visual ranking.

Figure 9 is a ternary diagram showing presently developed waste glasses plotted according to their simplified compositions of network formers, network modifiers, and intermediates. Following classical theory of glass structure, the concentrations of silica, boron oxide, and phosphorus oxide were summed as formers, the alkali and alkaline earth oxides were lumped as modifiers, and all other oxides were considered intermediates. Glasses developed for wastes at each of several U.S. sites define an area on the ternary field. The positions of these specific glass fields is somewhat indicative of the comparative properties of the corresponding glasses. For instance, Rockwell's glasses melt at relatively high temperatures. This is logical, since the Rockwell field contains more glass-formers than do the others.

The generic study will be limited to glasses in the large field defined by points a, b, c, d, e, and f. Predictability for properties of glasses within this field would streamline the development of glass formulations for most nuclear wastes. Before a study of the entire field is attempted, the method will be tested on a smaller field involving approximately ten oxide components with narrowed concentration ranges.

TABLE 3. Twenty-Six Components for Generic Study

	Study Values, mole%	
Oxide	-	+
Formers		
SiO_2	29	70
B_2O_3	6	17
P_2O_5	0	2.6
Modifiers		
Li_2O	0	20
Na_2O	5	24
K_2O(a)	0	5.5
MgO	0	8
CaO	0	18
SrO(a)	0	6.5
Cs_2O	0	2
Intermediates		
Al_2O_3	0	22
TiO_2	0	7.5
ZrO_2	0	4
Cr_2O_3	0	3.5
MnO_2	0	5
Fe_2O_3	0	12
NiO	0	4.5
ZnO(a)	0	10
MoO_3(a)	0	2.8
RuO	0	1.5
PdO(a)	0	1
TeO_2	0	0.5
Bi_2O_5	0	3.3
Gd_2O_3	0	4.3
CeO_2(a)	0	1.8
U_3O_8	0	0.8

(a) Representative of group.

TABLE 4. Grouped Oxides for Generic Study Represented by Major Members

Elemental Group	Mean Proportion in Group
Potassium group	
K_2O(a)	73
Rb_2O	3
Cs_2O	24
Strontium group	
SrO(a)	73
BaO	27
Zinc group	
CuO	22
ZnO(a)	78
Molybdenum group	
MoO_3(a)	89
Tc_2O_7	11
Palladium group	
Rh_2O_3	21
PdO(a)	79
Gadolinium group	
Y_2O_3	8
La_2O_3	20
Nd_2O_3	30
Sm_2O_3	5
Gd_2O_3 (a)	37
Cerium group	
CeO_2(a)	67
ThO_2	27
NpO_2	6
PuO_2	1

(a) Representative of group as variable generic study.

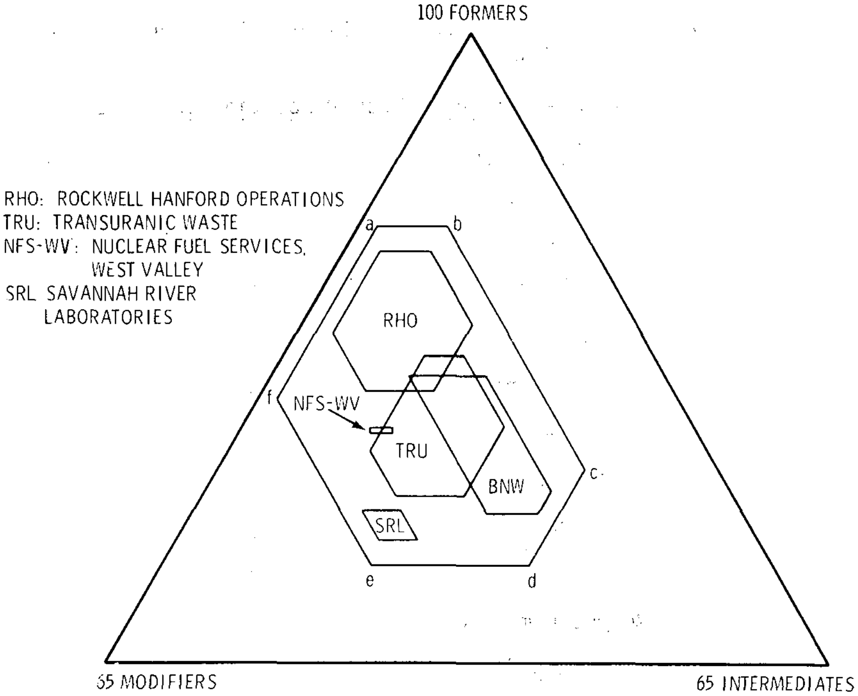

FIGURE 9. Waste Glass Regions and Experimental Fields

LEACH RATES AT HIGH TEMPERATURES AND PRESSURES - J. H. Westsik, Jr. and R. P. Turcotte

This quarter we have been writing a PNL document entitled "Hydrothermal Reactions of Nuclear Waste Solids - A Preliminary Study." The summary from this report follows.

Report Summary

A simulated high-level waste glass, supercalcine, and some common ceramic and metallic solids were exposed to hydrothermal conditions at 350°C and 250°C for time periods ranging from three days to three weeks.(a) Most of the experiments were done in salt brine, but the glass study did include deionized water tests so that the influence of salt could be better understood.

Under the extreme hydrothermal conditions of these tests, all of the materials examined underwent measurable changes. The glass is converted to a mixture of crystalline phases, depending upon conditions, giving $NaFeSi_2O_6$ as the primary alteration product. The rate of alteration is higher in deionized water than in salt brine; however, under equivalent test conditions, 66% of the cesium originally in the glass is released to the salt brine, while only 6% is released to deionized water. Rubidium and molybdenum are the only other fission product elements significantly leached from the glass. Evidence is presented which shows that sintered supercalcine undergoes chemical changes in salt brine that are qualitatively similar to those experienced by glass samples. High concentrations of cesium enter the aqueous phase, and strontium and molybdenum are mobilized.

(a) These conditions were selected to accelerate the hydrothermal reaction; actual temperature during waste storage, even for a high-activity waste, should be less than 200°C if water is present during the first 100-yr time period following closure of the repository. At 1000 yr the temperature will be less than 100°C for both wet and dry storage.

Scouting tests were made with a variety of materials including commercial glasses, granite, UO_2, Al_2O_3, steel, and waste glasses. Weight losses under hydrothermal conditions are in a relatively narrow band, with glass and ceramic materials showing 3 to 20 times greater weight losses than 304L stainless steel in the 250°C test used.

The conclusion from these studies is that virtually all solid materials show hydrothermal reactivity at temperatures between 250°C and 350°C, and that these extreme conditions are not desirable. Further work is needed to establish kinetic parameters for the hydrothermal reactions.

GEOLOGIC MATERIALS: IMPLICATIONS FOR RADIOACTIVE WASTE DISPOSAL - R. C. Ewing

Volcanic glasses, the most common of the naturally occurring glasses, are very often altered by weathering and leaching and recrystallize to their fine-grained compositional equivalents (rhyolites and felsites). The oldest reliably dated volcanic glasses are 40 million years old, but the majority of the dated glasses are much younger. Experimental studies of volcanic glasses have produced devitrification textures. Laboratory experiments as well as empirical measurements have determined hydration rates for volcanic glasses as a function of composition, temperature and climate. The presence of water and the temperature are the most important rate-controlling variables. Even material that still may be described as glassy often exhibits evidence of alteration and recrystallization.

Despite the common alteration and recrystallization effects observed in volcanic glasses, glasses formed as a result of impact, tektites and lunar glasses may occur in a substantially unaltered form. In the case of tektites, their resistance to alteration is a result of their high SiO_2 content and low alkali content. Lunar glasses have been preserved for hundreds of millions of years because they exist in an environment with a low oxygen fugacity and an extremely low water vapour partial pressure. Thus, one might expect glasses of particular compositions or in specific types of environments to be stable for long periods of time.

It is difficult and inappropriate to make direct comparisons between naturally occurring glasses and glass waste forms, as their compositions and thermal histories are very different; however, natural glasses may serve as standards of comparison for laboratory experiments designed to evaluate the long-term stability of synthetic glass waste forms.

It is interesting to speculate on the behavior of volcanic glasses when subjected to potential waste repository conditions. Data in the literature suggest the following behavior for conditions as specified, with an activation energy equal to 50 kcal/mole and a frequency factor of 10^{20} microns/million years for volcanic glass:

0 to 30 Hours; 900°C to 400°C; Anhydrous

Minimal devitrification effects observed. Rate of cooling too great for substantial nucleation or crystallite growth.

30 Hours to 20 Years; 400°C to 300°C; Anhydrous

Complete devitrification in 1700 years at 400°C or 10^6 years at 300°C.

20 Years to 200 Years; 300°C to 60°C: Hydrous

Hydrothermal reconstruction in less than ten years at 300°C or 10^8 years at 100°C. Extensive alteration as a result of cation exchange reactions.

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

During the past reporting period stored energy, density, and x-ray diffraction measurements have continued on the one vitreous and two devitrified waste glasses (77-260 waste glass) doped with 2 wt% ^{244}Cm. Optical metallography and SEM analysis of these waste glass forms have also been conducted. At the present time the accumulated alpha dose is 6×10^{17} α/g, equivalent to approximately 80 years' storage.

The density changes as a function of accumulated alpha dose are shown in Figure 10. In the vitreous glass there is a small positive change in density; in both devitrified glasses the density changes are much larger and are negative. The greatest density change observed has been in the devitrified waste glass cooled at -6.25°C/hr; in this glass, the density change has reached a value of -0.75%. In the glass devitrified at 700°C for 1 week, the results indicate that the density change may have reached saturation at -0.4%.

Energy dispersive x-ray analysis on the SEM suggests that the ^{244}Cm is uniformly dispersed in the vitreous glass. Similar analysis of each devitrified glass indicates that the glass matrix is depleted in ^{244}Cm, while the devitrification products are enriched in ^{244}Cm. The results also show that the devitrification products, $Gd_2Ti_2O_7$ and a phase high in gadolinium, calcium and phosphorous, (likely a complex phosphate) have approximately the same ^{244}Cm content; therefore, the potential radiation damage occurring in both devitrification products should be the same.

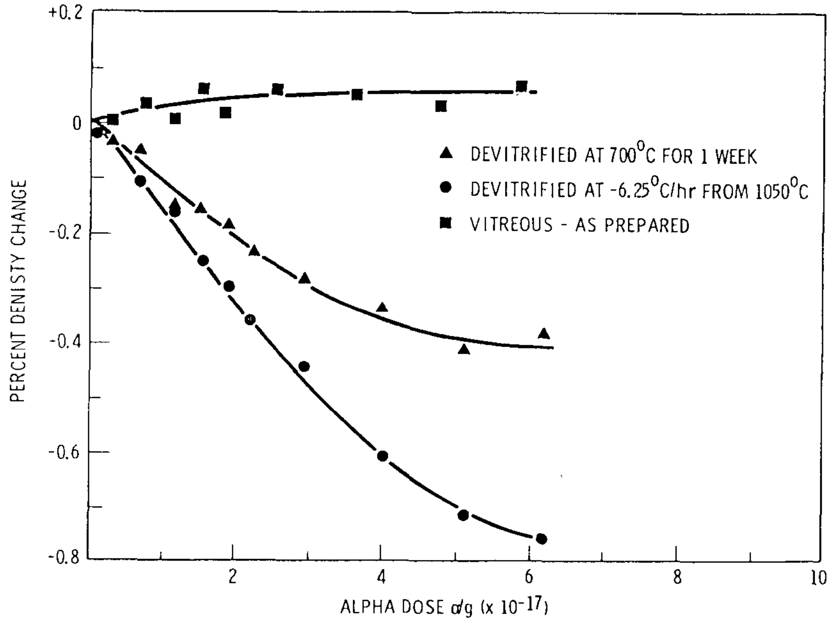

FIGURE 10. Density Change as a Function of Alpha Dose in 77-260 Waste Glass Doped with 2 wt% ^{244}Cm

X-ray diffraction analysis of both devitrified waste glasses indicates that the unidentified Gd-Ca-P phase is undergoing a crystalline-to-amorphous transformation as a result of radiation damage. The decrease in the diffracted intensity ratio, I/I_0, as a function of alpha dose, is shown in Figure 11 for this particular phase. The optical micrograph shown in Figure 12 also shows the severe deterioration of the Gd-Ca-P phase. The $Gd_2Ti_2O_7$ is found to be relatively resistant to radiation damage, with no significant changes in the diffracted x-ray intensity observed thus far. In the case of the vitreous glass, no changes in the x-ray diffraction pattern have been observed.

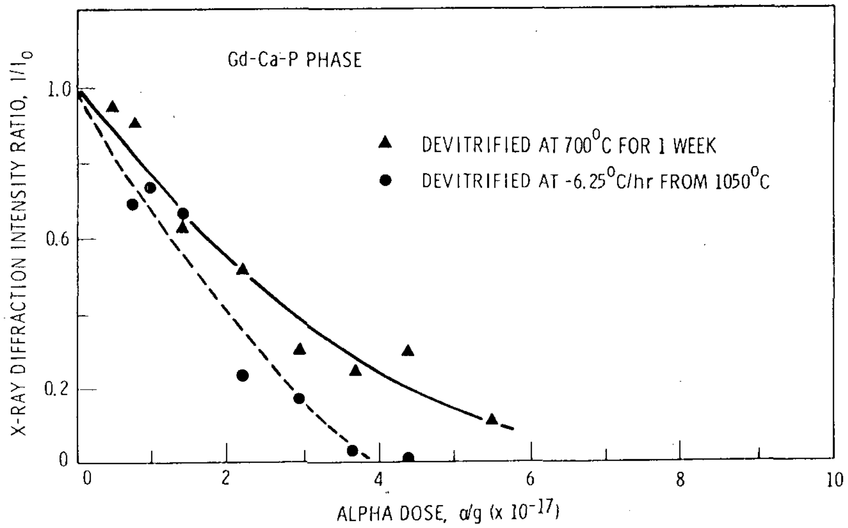

FIGURE 11. Diffracted X-Ray Intensity as a Function of Alpha Dose for Gd-Ca-P Phase in Devitrified 77-260 Waste Glass Doped with 2 wt% ^{244}Cm

FIGURE 12. Microstructure of 77-260 Waste Glass Doped with 2 wt% ^{244}Cm and Slow-Cooled at -6.25°C/hr [(a)]

(a) The light phase is $Gd_2Ti_2O_7$; the darker phase is a Gd-Ca-phosphate phase which shows severe deterioration. The alpha dose is 4 x 10^{17} α/g.

PHASE BEHAVIOR - J. W. Wald

Qualitative phase analysis on a high-sodium, high-gadolinium glass (composition 77-260) has been conducted over the last reporting period. Initial phase analyses for this glass composition appear in Table 5.

TABLE 5. Crystalline Phases Identified in Glass 77-260

Phase	Description
RuO_2	Melt insoluble
$NiFe_2O_4$	Melt insoluble from crucible spallation
$Gd_2Ti_2O_7$	Primary devitrification phase at short times and high temperatures
Gd/RE-Ca-Phosphate	Primary devitrification phase ingrowing at long times and low temperatures

Levels of percent crystallinity as a function of annealing temperature for times extending to two months appear in Figure 13. The percent crystallinity values are mainly controlled by the early formation of $Gd_2Ti_2O_7$ at short times (1 da → 1 wk) in the temperature range 750°C → 800°C and the later formation of the Gd/RE-Ca-phosphate phase (600°C) at the expense of the $Gd_2Ti_2O_7$ phase (800°C).

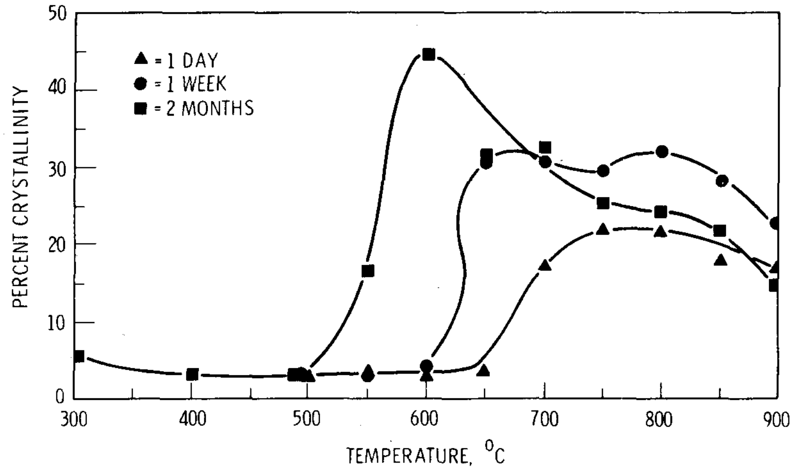

FIGURE 13. Total Crystal Yield for Waste Glass 77-260 as a Function of Holding Temperature for 1 Day, 1 Week, and 2 Months' Time

THERMAL AND MECHANICAL SHOCK - L. R. Bunnell

Size analysis of the simulated waste glass in three large canisters filled by the ceramic melter was completed. The canisters were:

CM-1 = 0.40 m in dia x 2.74 m long
CM-3 = (KT-23), 0.61 m in dia x 2.44 m long
2-H = 0.91 m dia x 2.74 m long

The surface-area-to-weight ratio of the glass was computed using an assumption of perfect spheres. This number was 0.63 cm^2/g for CM-1, 0.91 cm^2/g for the outer portion of CM-3, and 0.56 cm^2/g for 2-H. The surface-area-per-gram value is a factor of some interest, since it can in turn be used to calculate the ratio of the surface area including cracks to that of an uncracked body of the same dimensions. This ratio was 18.1 for CM-1, 27.4 for CM-3 and 33.9 for 2-H. The trend toward larger ratios with canister size results from the relative constancy of the surface area per gram, combined with the lower surface/volume ratio at larger canister diameters. A given ratio of surface area to volume occurs at a single radius for a sphere. At a ratio of 0.63 cm^2/g(CM-1) the radius is 1.6 cm. An equivalent calculation for 2-H yielded r = 1.8 cm.

The respirable portion of CM-3 was determined by sedimentation size analysis, and was 2.71×10^{-3} by weight. Sedimentation size analysis was also done for can KT-14, which was the same diameter as CM-3, weighed 2000 kg, and was dropped 7.62 m onto a concrete pad. The respirable portion amounted to only 0.13% of the highly damaged glass in the impact zone, which was estimated to comprise about 12% of the total glass volume. Examination of another similarly impacted canister is proceeding to better determine the extent of the damaged zone.

Three natural glasses provided by Dr. R. Ewing of the University of New Mexico were impacted at 160 ft-lb (217 joules). These glasses are of three different ages, as shown in Table 6 below.

TABLE 6. Sample Designation and Age of Natural Glasses

Sample No.	Age, yr
77-GM-01	500
77-OM-01	5000
72-G-004	670,000

Figure 14 shows the sieve analysis of the glass, and also includes soda-lime-silica glass as a comparison. Two of the three are quite similar to soda-lime glass (and hence to candidate waste glasses), while the third was substantially less friable than the rest. The oldest glass ranks as least friable, though composition differs little among the three. Silica content is between 70% and 80%, as compared to 72% for soda-lime-silica glass.

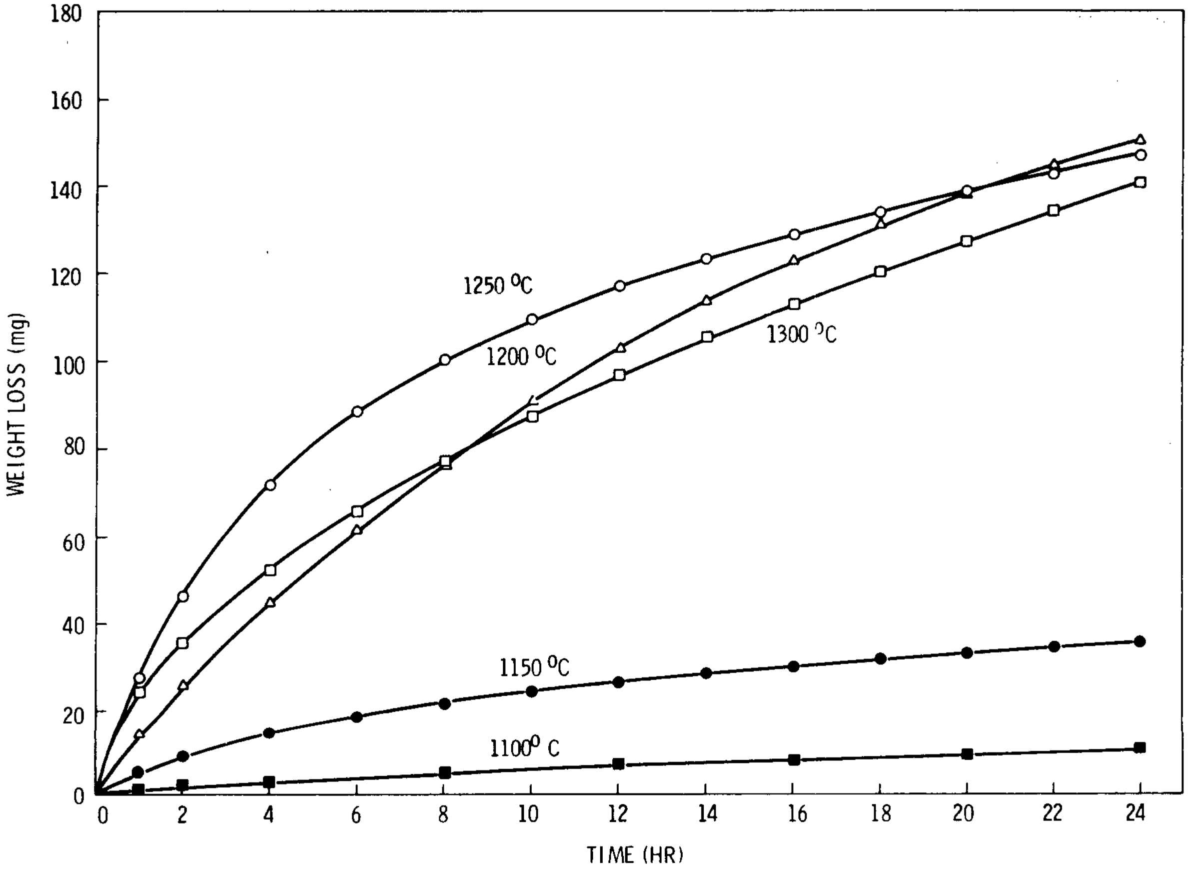

FIGURE 14. Sieve-Sizing Data for Three Natural Glasses Impacted @ 160 ft-lb Compared to Soda-Lime-Silica Glass

SECTION 3 - ALTERNATIVE WASTE FIXATION PROCESSES

The goal of this task is to develop alternative waste fixation procedures that will serve as viable backup processes. Cost and safety factors of the alternative processes and products are to be compared to those of the current reference process and product--silicate glass castings in large metal canisters. These alternative processes are being developed on the laboratory scale. In the concept currently emphasized the waste is formed into small granules or pellets that are coated with nonradioactive, inert materials to provide containment and leach resistance. The coated waste shapes are then incorporated into a metal matrix that provides impact resistance and increased thermal conductivity.

THE PENNSYLVANIA STATE UNIVERSITY SUPERCALCINE INVESTIGATIONS - G. J. McCarthy, Program Leader

The nature of the Penn State participation in the Advanced Waste Forms Program and the supercalcine-ceramics concept have been described in previous reports. During the last quarter, much of the principal investigator's time was committed to a special writing assignment for the Department of Energy. Research progress during this period included initiation of crystal chemical and compatibility studies for Thorex waste supercalcine development, completion of thermal stability runs on the sodalite structure solid-solution phase [So_{ss}], and completion of phase behavior studies in several sub-systems of the fluorite structure solid-solution system U-Th-Ce-Zr-O.

Thorex Waste Supercalcine-Ceramics - G. J. McCarthy and D. E. Pfoertsch

Development of the Thorex waste supercalcine-ceramics was initiated during the last quarter. In reviewing Thorex high-level liquid waste (HLLW) compositions, it was noted that the only elements not included in current supercalcine formulations are potassium, thorium, and fluorine. There are about 6 mole% potassium, 4 mole% thorium and 22 mole% fluorine in formulation TW-3. Potassium should crystallize in the pollucite phase. Thorium should crystallize in one of the U or RE supercalcine host phases and is not expected to present any difficulty. Nature offers us two refractory and low-solubility minerals of fluorine--fluorite (CaF_2) and fluorapatite ($Ca_{10}[PO_4]_6F_2$). Both of these minerals are isostructural with current supercalcine host phases, so the possibility of mutual solid solutions looks promising. Much of our early work on Thorex waste supercalcines will be focused upon finding a suitable host phase for fluorine that can be prepared by routine supercalcine processing. This will involve crystal chemical investigations of the solid solution between oxide and fluoride F_{ss} and A_{ss} phases, as well as compatibility studies.

Three potential F-fixation roles are currently being studied:

i. crystallization as fluorite (CaF_2) by appropriate additions of calcium,

ii. crystallization in the halide sites of alkaline earth-rare earth-silicate apatite solid solution [A_{ss}] phases,

iii. crystallization as fluorapatite ($Ca_{10}[PO_4]_6F_2$) by appropriate additions of calcium and phosphate.

The first and third phases are, of course, well known minerals, and the second phase has been reported. However, the two relevant questions here are:

i. Can the phases be formed by typical supercalcine-ceramics processing (calcination, pelletization, air firing at 1000° to 1200°C for crystallization-consolidation)?

ii. Will these phases be compatible with other established supercalcine phases (e.g., the pollucite, scheelite, monozite phases)?

These questions are being addressed and progress will be described below. Also described will be several compatibility runs involving the monozite [M_{ss}] phase and an examination of the pollucite phase as it would be formed in the high-potassium Thorex waste supercalcines.

Compatibility of CaF_2 with Established Supercalcine Phases.

Clearly, the simplest way to fix fluorine in supercalcine-ceramics would be as CaF_2, a refractory (m.p. = 1423°C) and low-solubility ($K_{sp} = 4 \times 10^{-11}$ m/l at 26°C) phase. However, CaF_2 is a well known metallurgical and ceramic flux for oxides and this raises doubts about its potential for compatibility with key supercalcine phases such as pollucite. Therefore, compatibility studies were the first requirement in evaluating this F-fixation phase.

The following compatibility pairs were tested at 1050° and 1200°C for 4 and 48 hr in air:

$CaF_2 + (K_{0.7}Cs_{0.3})AlSi_2O_6$ [P]
$CaF_2 + (SR_{0.4}Ba_{0.3}Ca_{0.3})MoO_4$ [S_{ss}]
$CaF_2 + REPO_4$ [M_{ss}]
$CaF_2 + ZrO_2$
$CaF_2 + Fe_2O_3$
$CaF_2 + (Th_{0.6}U_{0.1}Ce_{0.3})O_{2+x}$ [F_{ss}].

The appropriate amounts of Ca, K, Cs, Al, Sr, Ba, Th, RE, Ce, (ZrO_2), (UO_2) and Fe nitrates, colloidal silica (Ludox), and NH_4F solutions were mixed, dried and calcined at 600°C. The calcined powder was ground, pelletized and fired in small Pt cups. After firing at 1050° and especially 1200°C, many of the pellets had either melted or vaporized (the pellet was gone). Interpretation of the x-ray diffraction results on the products is not complete, but it can be stated that in no case was the CaF_2 phase present.

The fluorite apparently has assumed its usual role as a flux and is clearly unsuitable as a F-fixation phase in supercalcines.

Calcium-Rare Earth-Silicate-Fluorapatite.

One very likely crystal chemical role for Thorex waste fluorine in supercalcine-ceramics is the halide site of the apatite structure solid solution phase [A_{ss}]. There are several literature reports of syntheses of $AE_4La_6[SiO_4] \cdot 6F$ (AE = Ca, Sr) by familiar ceramic methods involving the mixing and firing of powders. A scouting experiment was made to see if there would be any difficulty in preparing such an A_{ss} phase by the usual supercalcine processing.

Solutions of $Ca(NO_3)_2$, $Nd(NO_3)_3$, Ludox and NH_4F in the molar ratio for $Ca_4Nd_6[SiO_4] \cdot 6F_2$ were dried at 110°C and calcined at 600°C. The resulting powder was ground, pelletized and fired at 900°, 1000°, 1100° and 1200°C for 6 and 24 hr in air. A phase-pure A_{ss} x-ray diffractogram was obtained from the 900° and 1000°C, 6-hr firings but a few extra weak reflections were noted in 24-hr firing. The 1100° and 1200°C firings gave a mixture of A_{ss} and an as yet unidentified second phase. These results indicate that the phase $Ca_4Nd_6[SiO_4] \cdot 6F$ can be synthesized by supercalcine processing methods using a crystallization temperature of 900° to 1000°C, but this phase may decompose slowly during additional firing at these temperatures. The phase is not stable under these conditions at 1100° to

1200°C. Specimens are currently being analyzed for fluorine to see whether its volatilization could be the mechanism for the instability at 1100° to 1200°C. This study will be extended to A_{ss} phases with AE = Sr, Ba and RE = La, Gd, Y, and to phosphate-silicate A_{ss} solid solutions.

Monazite Solid Solution [M_{ss}].

With the possibility that Thorex supercalcines will involve substantial phosphate additions, as well as the potential desirability of crystallizing rare earths and actinides in this phase to avoid radiation effects, it is necessary to examine the formation, solid-solution behavior and compatibility of the monazite solid-solution phase.

One important compatibility question is: which RE phase is more stable, the silicate A_{ss} phase or the phosphate M_{ss} phase? If the silicate were more stable, then it would always form in aluminosilicate supercalcines no matter how much phosphate was added. The compatibility study can be expressed as follows:

$$8RE + 8[PO_4] + 2Ca + 6SiO_2 \begin{array}{l} \nearrow 8\,REPO_4\,[M_{ss}] + \text{Ca-silicates} \\ \\ \searrow Ca_2RE_8[SiO_4]_6O_2\,[A_{ss}] + 4P_2O_5\,. \end{array}$$

The experiments, using the usual supercalcine processing conditions and 1050° and 1200°C/6-hr and 48-hr firings demonstrated unambiguously that the RE has a greater affinity to crystallize in the monazite than in the apatite phase. This means that phosphate-rich supercalcine formulations can be developed for either Purex or Thorex wastes as required.

Pollucite-Leucite in Thorex Waste Supercalcines.

Thorex wastes are richer in potassium than in cesium. Our first phase formation models would call for co-crystallization of cesium and potassium in a solid solution phase intermediate in composition between pollucite ($CsAlSi_2O_6$) and leucite ($KAlSi_2O_6$). A typical thorex waste formulation indicates that this phase would have the approximate composition:

$$(K_{0.65}\,Cs_{0.25}\,Rb_{0.07}\,Na_{0.03})AlSi_2O_6.$$

We have modeled this phase with the composition $(K_{0.7}Cs_{0.3})AlSi_2O_6$ and synthesized it by the usual supercalcine processing conditions. The x-ray diffractogram of the product strongly resembled pure cubic pollucite, except that some splittings and extra reflections indicated the presence of the lower symmetry that would be expected from substitution of the smaller potassium for cesium.

Thermal Stability of Molybdate-Containing Sodalite Phase - R. G. Johnston and G. J. McCarthy

The background and methodology for these thermal stability measurements were covered in previous quarterly reports.

A sodalite phase having the composition $Ca_2Na_6Al_6Si_6O_{24}MoO_4$ was synthesized and studied by thermo-gravimetric analysis (TGA). The specimen was heated from room temperature to 1300°C at a rate of 3.3°C/minute and then left at 1300°C for 12 hours. No significant weight loss was noted up to ~1250°C. After 12 hours at 1300°C, the total weight loss for the dynamic and isothermal TGA was about 1.9%. Thus, the sodalite phase is a surprisingly refractory host for molybdate in supercalcine.

Phase Relations in the System U-Th-Ce-Zr-O in Air - J. G. Pepin and G. J. McCarthy

Emphasis during the last quarter has been on the binary and ternary sub-systems of the quinary system. The 1200°C isothermal phase relations for each binary, and the U_3O_8-ThO_2-ZrO_2 ternary, have been completed. Phase diagrams and plots of fluorite structure solid solution [F_{ss}] cell parameter isopleths are available from the authors or J. M. Rusin of PNL.

GLASS-CERAMICS DEVELOPMENT - L. A. Chick

A celsian glass-ceramic frit developed at the Hahn-Meitner Institute in Berlin was duplicated and combined with 20 wt% PW-9 calcine to produce glass-ceramic samples for characterization at PNL this quarter. Four samples were prepared with different heat treatment procedures. Figures 15 through 18 are SEM photos of typical areas in the four samples. Various forms of celsian phase ($BaAl_2Si_2O_8$) were identified by energy dispersive x-ray analysis and x-ray diffraction. These are identified as points "C" in the figures. Similarly, a barium molybdate phase ($BaMoO_4$) was identified and is shown at points "B." Evidence of other phases is present but is not yet confirmed.

Development of two new glass-ceramic formulations will continue next quarter.

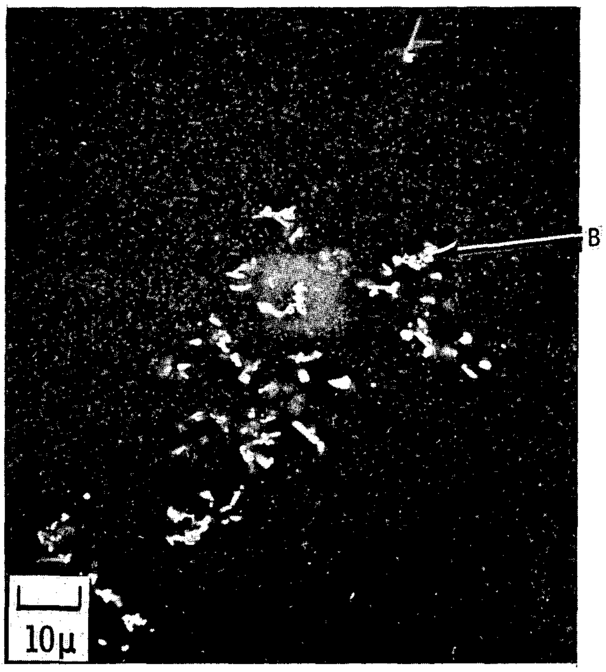

FIGURE 15. Parent Glass-Ceramic Sample Melted at 1250°C for 2 hr; Annealed at 550°C for 2.5 hr

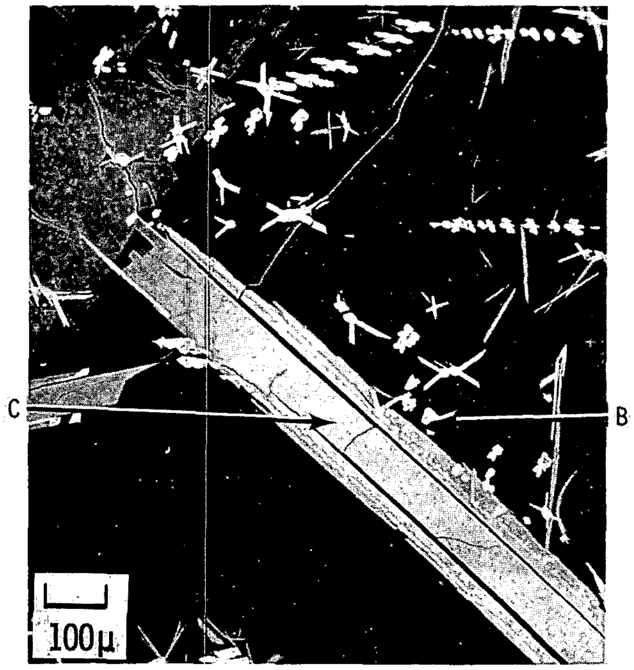

FIGURE 16. Slow-Cooled Glass-Ceramic Samples Cooled from 1000°C at 6.25°C/hr

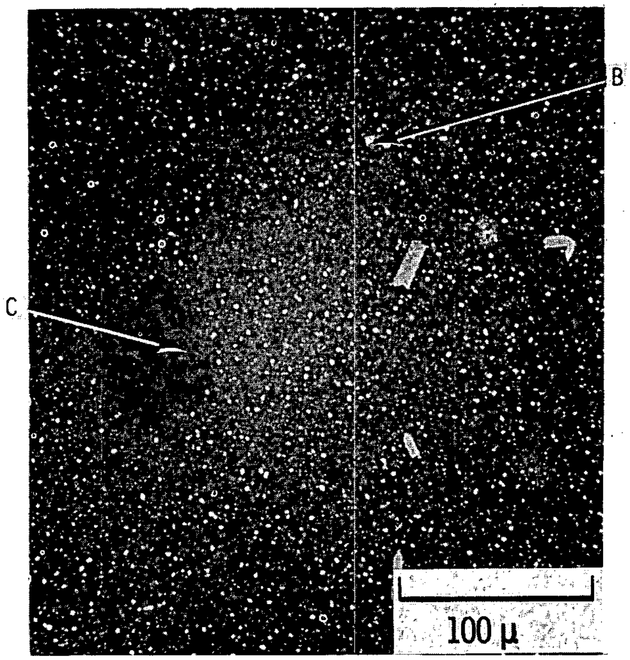

FIGURE 17. Glass-Ceramic Sample After Two-Stage Heat Treatment: Nucleation at 600°C, 3 hr; Growth at 800°C, 12 hr; Annealing at 550°C, 3 hr

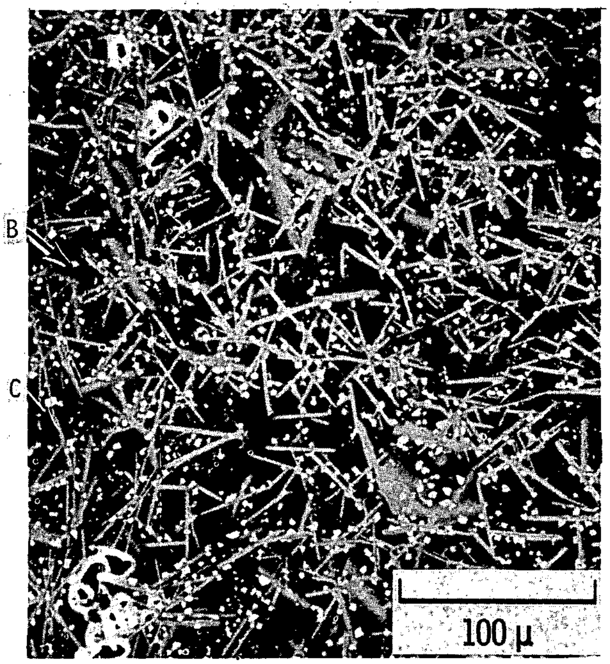

FIGURE 18. Glass-Ceramic Sample After 2-hr Cool (1000°C to Room Temp. in 2 hr)

IMMOBILIZATION OF RADIOACTIVE WASTES IN CONCRETE - R. O. Lokken

Concrete is used for the immobilization of low-level wastes and has been considered for use in the immobilization of higher-level wastes (Colombo and Neilson, Jr. 1976; Stone 1977; International Atomic Energy Agency 1968). Although the application of concrete immobilization to HLLW is problematical, it was of interest to examine in a preliminary way the effects of incorporating a well studied HLW calcine, PW-7a, in concrete. An experimental program for the preparation and evaluation of waste forms composed of nonradioactive HLW calcine and hydraulic cements is ongoing at Cascade Testing Laboratory, Bellevue, Washington. The objective of this program is to prepare calcine-cement samples for measurement of compressive strength, impact resistance, leachability, thermal conductivity, etc., and to identify any extreme incompatibilities of the calcine and cement during mixing and curing under various conditions. Cascade Testing Laboratory is preparing calcine-cement mixes and performing measurements of water/solids ratio, mix set time, compressive strength, weight loss, density, and temperature generated by hydration reactions. A typical cement curing exotherm is presented in Figure 19.

Samples are being supplied to PNL for determination of impact resistance, leachability, and microscopic evaluation of reactions between cement and calcine particles. The results of these evaluations will be related to variations of cement type (high-alumina cement and Type II Portland Cement), simulated PW-7a calcine content (0, 5, 10, 20, and 30 wt%), and temperature.

Initial attempts at casting and cement-calcine mixes into 1-in.-dia by 5-in.-long cylinders resulted in products with air bubbles due to insufficient vibration during casting. These samples are being recast. Samples received by PNL for testing include:

- 100% Type II Portland Cement
- 95% Type II Portland Cement
  5% simulated PW-7a calcine
- 90% Type II Portland Cement
  10% simulated PW-7a calcine
- 80% Type II Portland Cement
  20% simulated PW-7a calcine
- 70% Type II Portland Cement
  30% simulated PW-7a calcine

These samples will be prepared for thermal conductivity determination. All samples will be fabricated by the end of next quarter.

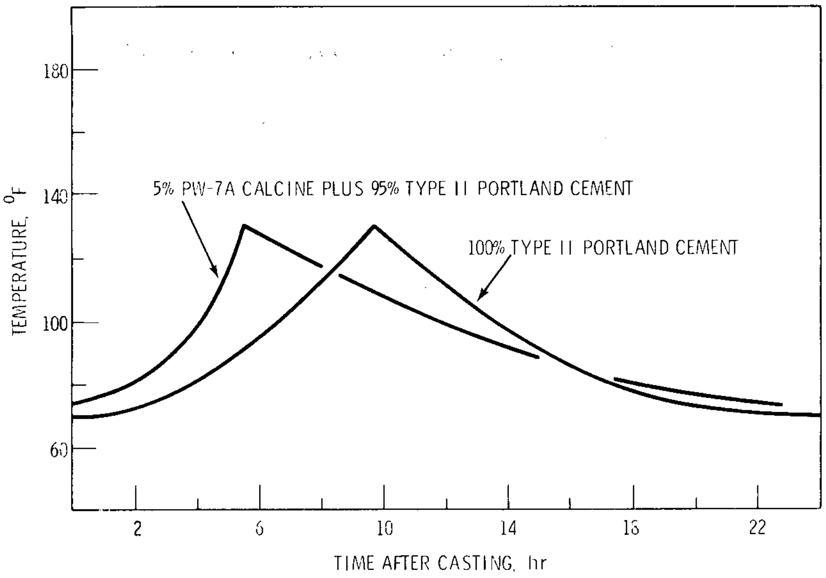

FIGURE 19. Temperatures Resulting from Hydration Reactions During the Curing of Cement Pastes(a)

(a) Samples are 4 in. in diameter by 5 in. long.

VAPORIZATION STUDIES - W. J. Gray

Supercalcine pellets 1.31 cm in diameter x 0.52 cm high and weighing 2.83 g were prepared by cold pressing and sintering for 1 hr at 1200°C, during which time they lost 31 mg of weight. The composition of the supercalcine (batch SPC-4) is given in Table 7. Volatility measurements on these pellets were conducted using equipment described earlier (Gray, 1976). During these measurements, the pellets were held in a platinum pan about the same height but slightly larger in diameter than the pellets.

Gross weight loss data are shown in Figures 20 and 21. Evidently some change takes place in the pellets at temperatures above 1200°C that reduces weight loss rates, particularly for long times, but the mechanism has not been identified.

Weight loss during pellet preparation, which involved firing for 1 hr at 1200°C, was relatively large. Therefore, vapors were collected and chemically analyzed. Table 8 shows results which are the average of two runs.

Vapors were also collected from the finished pellets during 4-hr runs in the range 1100° to 1200°C. Two vapor samples were collected and chemically analyzed at each temperature. Data shown in Figures 22 and 23 are the averages of these two samples. Note, also, that these losses are in addition to those listed in Table 8.

Data shown here are similar to that reported earlier (McElroy et al., 1979) for supercalcine batch SPC-2, whose composition was only slightly different than that of SPC-4.

TABLE 7. Composition of Supercalcine (SPC-4)

Constituent Waste Oxides	Weight Percent
Ag_2O	0.1
BaO	2.5
CdO	0.2
Cr_2O_3	0.5
Cs_2O	4.6
Fe_2O_3	4.8
MoO_3	8.2
Na_2O	0.2
NiO	0.2
P_2O_5	4.3
Rb_2O	0.6
RuO_2	0.5
SrO	1.7
ZrO_2	7.8
CeO_2	5.1
La_2O_3	1.4
Nd_2O_3	13.3
Pr_6O_{11}	0.3
Sm_2O_3	0.2
Gd_2O_3	16.6
Additives	
CaO	2.1
SrO	2.6
Al_2O_3	4.5
SiO_2	17.6

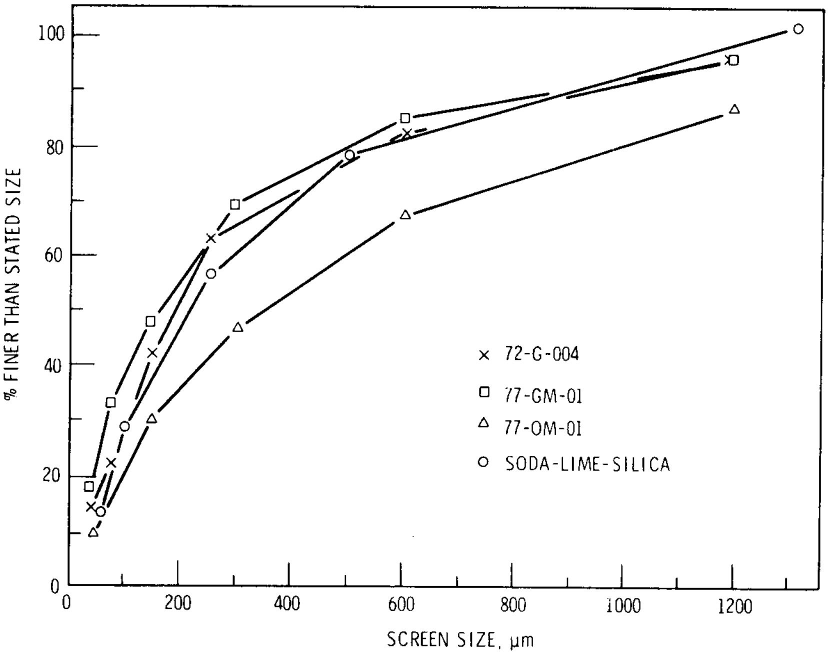

FIGURE 20. Weight Loss of Supercalcine (SPC-4) Pellets in Dry Air

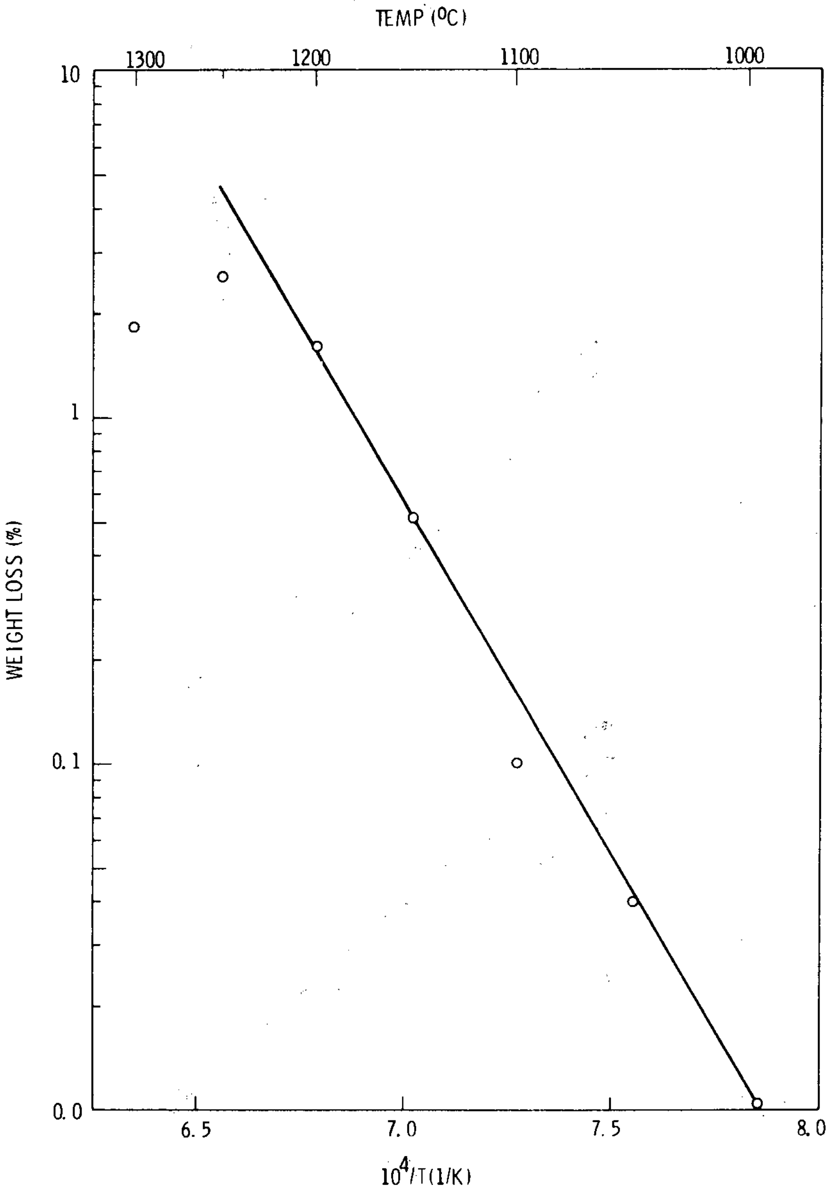

FIGURE 21. Weight Loss of Supercalcine (SPC-4) Pellets After 4 Hr in Dry Air

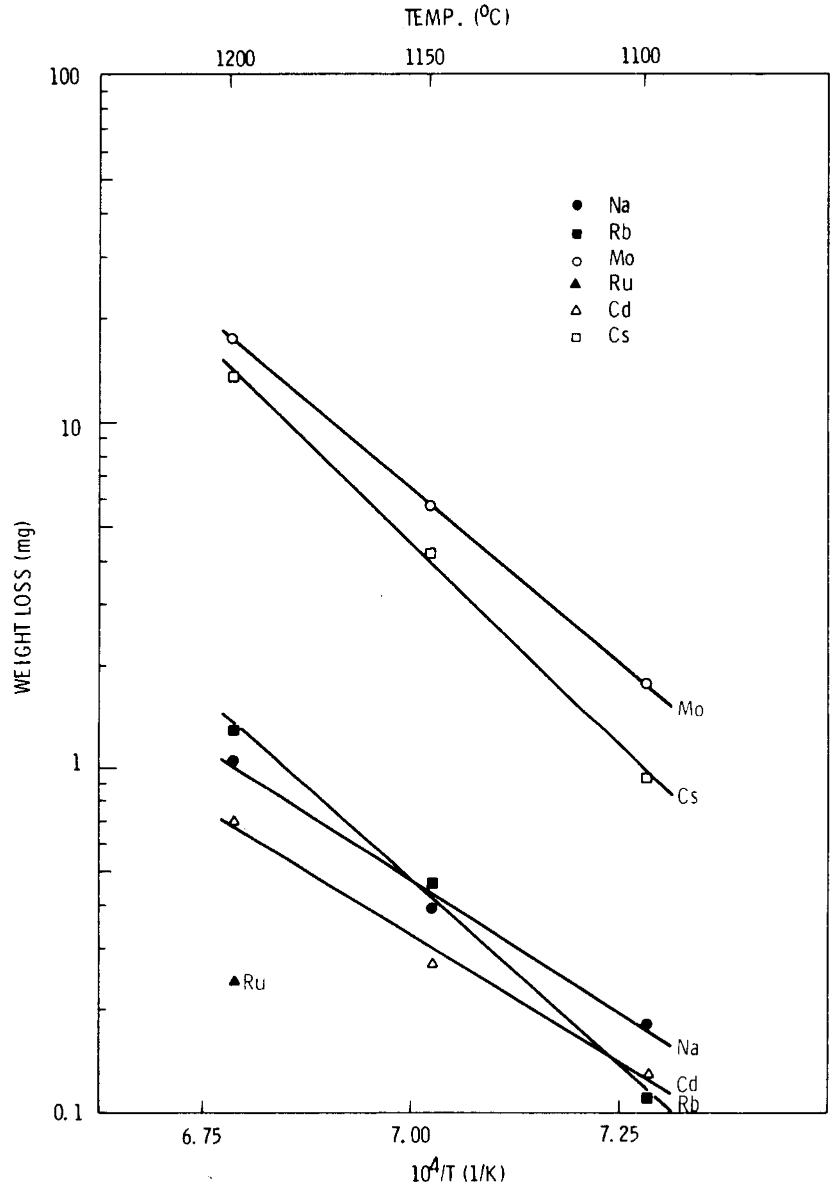

FIGURE 22. Absolute Weight Loss of Supercalcine (SPC-4) Pellets After 4 Hr

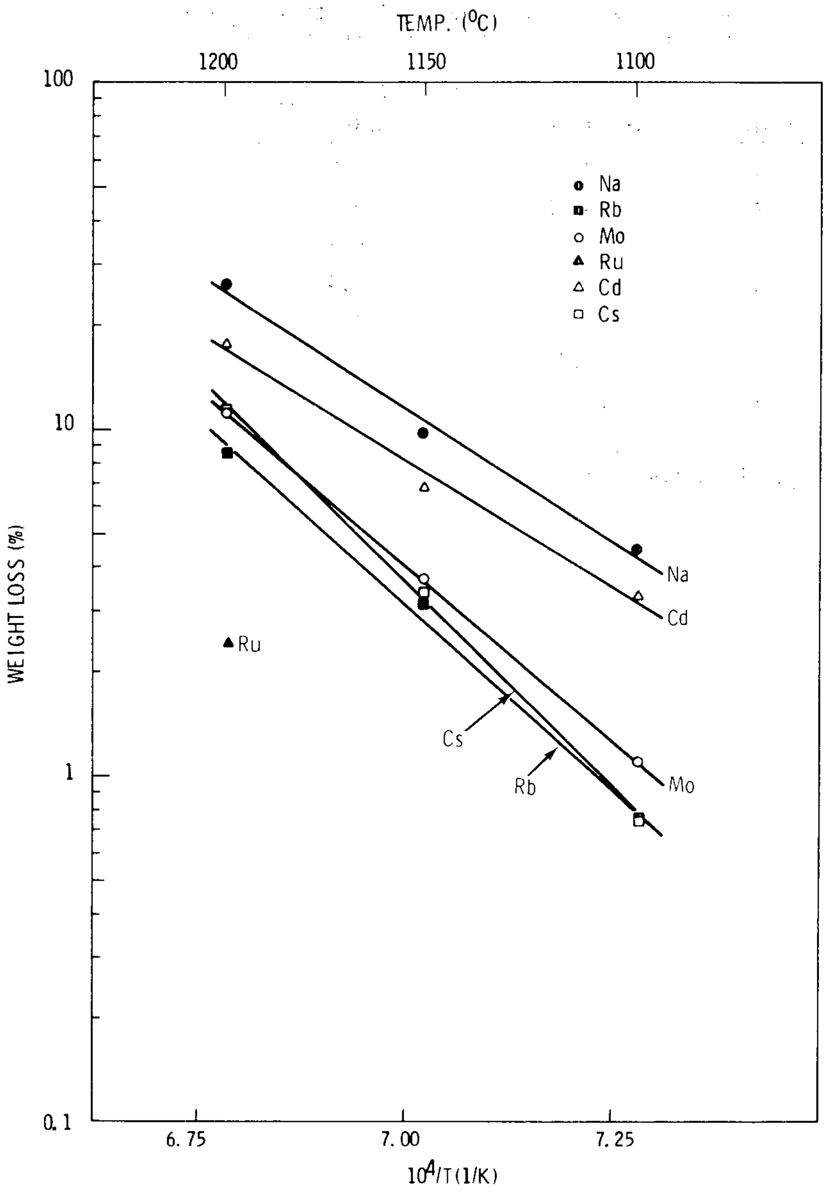

FIGURE 23. Fractional Weight Loss of Supercalcine (SPC-4) Pellets After 4 Hr in Dry Air

TABLE 8. Weight Loss of Individual Elements from Green Pellets of SPC-4 Fired for 1 Hr at 1200°C

Element	Weight Loss Absolute, mg	Relative, %[a]
Na	0.52	12.9
Rb	0.91	6.1
Mo	8.2	5.2
Ru	2.5	24.4
Ag	0.16	4.3
Cd	0.39	9.7
Cs	12.3	9.9

(a) Relative to amount originally present.

REFERENCES

Colombo, P. and R. M. Neilson, Jr. 1976. "Some Techniques for the Solidification of Radioactive Wastes in Concrete," Trans. Am. Nucl. Soc., 23, pp 161-162.

Gray, W. J. 1976. Volatility of a Zinc Borosilicate Glass Containing Simulated High-Level Radioactive Waste. BNWL-2111. Pacific Northwest Laboratory, Richland, WA 99352.

International Atomic Energy Agency. 1968. Treatment of Low- and Intermediate-Level Radioactive Waste Concentrates. Technical Report Series No. 82, STI/DOC/10/82, Vienna, Austria.

McElroy, J. L., J. E. Mendel, W. F. Bonner and M. H. Henry. Quarterly Progress Report - Research and Development Activities High-Level Waste Immobilization Program: January Through March 1978. PNL-2999-1, Pacific Northwest Laboratory, Richland, WA 99352.

Stone, J. A. 1977. Evaluation of Concrete as a Matrix for Solidification of Savannah River Plant Waste. DP-1448, Savannah River Laboratory, Aiken, SC 29801

PNL-2999-4

HLWIP QUARTERLY REPORT
OCTOBER THROUGH DECEMBER 1978

PNL-2999-4
UC-70

QUARTERLY PROGRESS REPORT
RESEARCH AND DEVELOPMENT ACTIVITIES
HIGH-LEVEL WASTE IMMOBILIZATION PROGRAM
OCTOBER THROUGH DECEMBER 1978

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May 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 October through December of 1978:

- A series of short-term tests performed with a laboratory-scale spray calciner (1 to 3 ℓ of liquid feed/hr) confirmed low volatility of ruthenium and cesium when calcining several waste compositions. Losses were 0.02 to 0.08% and 0.01 to 0.1% for ruthenium and cesium, respectively.
- The good resistance to devitrification of waste glass compositions 77-107 and 77-260 was demonstrated by measuring leach rates of thermally treated glass specimens. The leach rate of specimens held for 1 yr at a series of temperatures between 300° and 750°C did not increase over the leach rates measured on specimens held at similar temperatures for 2 months.
- A drop test of a non-heated canister filled with waste glass from the continuous melter resulted in fracture of glass throughout the canister, rather than only at the point of impact as is usually observed. Voids in the glass allowed the overall glass column to move, which increased fracturing. Heating the canister during filling will prevent void formation; such heating during filling is recommended.
- Carbon has been utilized as a coating in multibarrier waste forms and is being considered for other waste form applications. Preliminary results have shown very good leach resistance. The slight reaction that does occur is apparently an oxidation reaction. More experimentation is being done to better define the reaction.

PREVIOUS REPORTS

Previous reports in this series were BNWL-1699, -1741, -1761, -1788, -1809, -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 and -2999-3.

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JULY THROUGH SEPTEMBER 1978

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 FIXATION PROCESS DEVELOPMENT

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

EFFLUENT CONTROL - M. S. Hanson and C. A. Knox

The laboratory-scale spray calciner (LSSC) located in EDL-102 has been operating regularly. Besides fulfilling its primary objective of effluent analysis, the calciner is being used to test different feed compositions and to produce calcine for further studies. Typical operating parameters for the calciner are as listed in Table 1.

TABLE 1. Typical LSSC Operating Parameters

Parameters	Operating values
Calciner vacuum	-10 in. H_2O
Average feed rate	1-3 ℓ/hr
Nozzle feed pressure	20 psig
Nozzle atomizing air pressure	30 psig
Nozzle atomizing air flow	30 scfh
Barrel temperature	775°C
Cone temperature	130°C
Filter temperature	120°C
Nozzle temperature	40°C

A variety of compositions has been fed to the calciner, including SRP composite and fluoride-containing Thorex simulated feeds.

Our effluent analysis efforts have been focused primarily upon investigating potential corrosion problems in the process off-gas (POG) system. No significant corrosion has been seen in the off-gas system with any of the feed compositions tested.

A fully remote duplicate of the laboratory-scale spray calciner, along with the necessary feed and POG systems, has been designed and is presently under construction. This system will be installed in D-Cell, 324 Building, where it is to be used for effluent analysis from fully radioactive feeds.

Effluent analysis has been completed on a large number of nonradioactive spray-calciner/in-can melter operations. A variety of feed compositions was used, including PW-7A, PW-8, and TW-2. In general, the results show that:

- ruthenium losses to the POG system were low--on the order of 0.02% to 0.08%;
- cesium losses were also low--about 0.01% to 0.1%;

- strontium, which had previously been used as a measure of nonvolatile species loss, can no longer be used for this, since residual contamination is very high;
- gadolinium in the feed solution did not appear to increase ruthenium volatility;
- the addition of silicon metal as a reducing agent did not appear to affect ruthenium volatility.

SECTION 2 - WASTE FORM CHARACTERIZATION

The purpose of waste form characterization is to measure the properties of candidate solidified products and containers (solidified waste and canister) as functions of composition, processing parameters, and storage conditions. The measurements are used to: 1) ensure operability of the vitrification processes and 2) provide data for safety analyses of high-level waste management. The ultimate goal of waste characterization 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 a final disposal site, we may be fully confident that their behavior is understood and that any changes or interactions with their environments are wholly predictable.

THERMAL EFFECTS UPON STORED GLASS - J. H. Westsik, Jr.

One-year storage of specimens of 77-260 and 77-107 glasses at temperatures between 300° and 750°C has been completed. The Soxhlet leach rates shown in Table 2 indicate that the durability of the glasses did not change because of either the longer storage times or because of the storage temperature. Leach rates for shorter storage periods are reported in PNL-2265-4 (McElroy, 1979).

TABLE 2. Soxhlet Leach Test Results--One-Year Storage Samples of 77-107 and 77-260 Glasses

Storage Temperature, °C	Leach Rate in g/cm²-d, Based on Weight Loss in 72 hr 77-107	 77-260
300	2.5×10^{-5}	3.0×10^{-5}
400	4.0×10^{-5}	4.5×10^{-5}
500	3.7×10^{-5}	3.5×10^{-5}
550	2.7×10^{-5}	3.6×10^{-5}
600	3.4×10^{-5}	2.8×10^{-5}
650	4.3×10^{-5}	3.2×10^{-5}
700	4.0×10^{-5}	5.1×10^{-5}
750	3.0×10^{-5}	5.0×10^{-5}

STRESS AND CRACKING IN HIGH-LEVEL WASTE GLASS - S. C. Slate

During this period we prepared a report that discussed the causes and amounts of waste glass cracking which may be expected in large canisters (Slate, 1978). This report is a compilation of all currently available data from our glass tests. Conclusions of the report follow.

The major causes of cracking are thermal and residual stresses and impacts. Waste glass will crack when it is cast in large canisters. Under normal conditions, the additional surface area resulting from cracking is not available for environmental interactions because the pieces are tightly packed. Most of the cracking occurs near the canister surface and this is associated with a small amount of the total glass; 50% of the increased surface area occurs in about 1 wt% of the glass. Severe impact accidents will increase the surface area by factor of 4 to 10. Respirable particles will also be produced in an impact accident, but they will constitute <0.1 wt% of the fractured glass. The increase in surface area and number of respirable particles will not directly affect release levels. The canister and the facility or shipping cask is expected to contain the glass in all credible accidents. Additional studies on the effect of cracking on the waste management system are recommended, including continued evaluation of full-scale canisters and leach testing of large blocks of cracked glass.

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

The accelerated study of radiation damage effects in one vitreous and two partially devitrified forms of ^{244}Cm-doped 77-260 simulated waste glass is continuing. During the past reporting period density, x-ray diffraction, and stored energy measurements have continued and a second series of leach tests on samples receiving an accumulated alpha-recoil dose of 2×10^{18} α-R/cm^3 ($\sim$100 years equivalent storage time) have been completed. At the present time, the accumulated alpha-recoil dose in the glass samples is 3.1×10^{18} α-R/cm^2, which is equivalent to approximately 250 years' storage.

The density changes induced by the alpha-decay of ^{244}Cm have begun to saturate after 3×10^{18} α-R/cm^3. The density change in the vitreous glass has exhibited only a slight positive change (<0.1%). The largest density change has been in the devitrified glass cooled at 6°C/hr; in this glass the density change is negative and is beginning to saturate at a value of approximately -0.85%. In the glass devitrified at 700°C for 1 week, the density change has saturated at a value of approximately -0.47%.

Two major devitrification products are present in both devitrified glasses. One of the phases, identified as $Ca_3(Gd,Nd)_7(SiO_4)_5(PO_4)O_2$ with an apatite crystal structure, has undergone a complete crystalline-to-amorphous transformation in both devitrified glasses as a result of the radiation damage. The other major devitrification phase, $Gd_2Ti_2O_7$ with a cubic crystal structure, contains approximately the same ^{244}Cm content but remains relatively insensitive to radiation damage.

Leach rates based on Soxhlet and static pH4 and pH9 tests do not appear to significantly change with alpha-recoil dose--at least up to 2×10^{18} α-R/cm^3. The radiation-induced stored energy is saturating at levels below 50 cal/g.

PHASE BEHAVIOR - J. W. Wald

Microstructural examination of both HLW glasses and simulated glasses that were part of a comparative study highlighted briefly in the January-March 1978 HLWIP Quarterly (McElroy, Mendel, Bonner and Henry 1979) has not indicated any significant differences between the two systems. Most of the devitrification products predicted from studies with simulated materials also appear in the HLW glasses. The exceptions show the HLW glasses to actually be more devitrification-resistant than their simulated counterparts. Also, in the as-prepared condition there is less undissolved material in the case of HLW glasses. The high gamma field in the HLW glasses does not seem to change the devitrification behavior from that observed in the simulated nonradioactive glasses, either--at least not under the conditions studied. We conclude that the presence of a high gamma field does not alter devitrification kinetics significantly.

Bulk leach rates, based on the IAEA procedure, vary from one glass composition to another; however, the overall variance is only slightly over one order of magnitude. The devitrification treatment used was seen to increase the leach rate of the simulated glasses over that observed in the as-prepared condition, but this change was only on the order of about 2X. Leach rates for HLW glass samples will be reported as the data become available.

We began evaluation of an actinide doping experiment involving a simulated defense waste glass and two simulated power waste glasses this quarter. The technique involves the use of Cm-244, Am-243, Pu-239, and Np-237 as dopant species and α-auto-radiography as the method of evaluating actinide settling, agglomeration, or concentration in crystalline regions. Initial results have indicated that this technique is a strong tool in evaluating the ultimate disposition of the dopant species.

PHASE BEHAVIOR STUDIES - R. P. May and J. W. Wald

The vitrification/equilibrium behavior of the five defense waste glass compositions listed in Table 3 are currently being evaluated by means of the x-ray and scanning electron microscopy analysis of a series of remelt/anneals (from 750°C to 1150°C) and controlled cools from 1100°C. The experimental program is currently about 50% complete.

TABLE 3. Canister Data Summary

Major Components/glass	76-183-2	78-157	ICPP-ZR-101	SRP-411	RLB-14L
SiO_2	35.3	41.6	38.6	43.8	63.0
BeO_3	9.3	14.4	9.4	8.3	10.0
P_2O_5	3.2	0.7	1.3	-	-
CaF_2	-	0.3	18.3	-	-
Al_2O_3	1.0	3.6	5.9	11.7	5.8
Li_2O	-	2.0	1.3	9.4	2.0
Na_2O	11.5	8.6	16.0	9.4	17.3
K_2O	2.6	3.2	-	-	-
Cs_2O	-	1.0	-	-	0.4
CaO	2.0	3.2	2.1	5.0	-
BaO	0.8	3.6	-	-	-
TiO_2	6.0	-	-	-	0.9
ZrO_2	2.5	5.3	6.7	-	-
MaO_3	3.2	1.6	-	-	-
Fe_2O_3	2.4	1.8	-	8.0	-
CuO	3.0	-	-	-	-
ZnO	-	2.5	-	-	-
MnO_2	-	-	-	2.6	-
Rare Earths		Principal remainder			

For glass 76-183-2, eight crystalline phases have been tentatively identified in a devitrified specimen cooled at 7°C/hr from 1100°C. For isothermal anneals in the temperature range between 950°C and 1100°C, CeO_2 is the only detectable crystalline phase. Analysis of these specimens indicates that the greatest yield of CeO_2 occurs at about 1000°C. At 1100°C CeO_2 exists at 20% of its maximum value at 1000°C, and is all in glass solution at 1200°C. The vitrification kinetics/equilibrium of CeO_2, as well as other melt crystalline forms, will be studied as a part of this experimental program.

THERMAL AND MECHANICAL SHOCK - L. R. Bunnell

During preparation of a topical report on impact and strength testing of candidate waste-containing glasses, the plot in Figure 1 was produced. Some conclusions are:

- Fused SiO_2 exhibits the most fracturing upon impact.
- Both 76-101 and 73-1 frits are slightly superior to the corresponding waste glasses 76-68 and 72-68, respectively.
- The shape of the curves is very similar--the main difference being the amount of fine (-44 μm) particles produced.
- Soda-lime-silica glass is similar in performance to many candidate waste glasses.

Because of the availability of soda-lime-silica glass and its similarity in impact performance, it is a reasonable substitute for waste glasses.

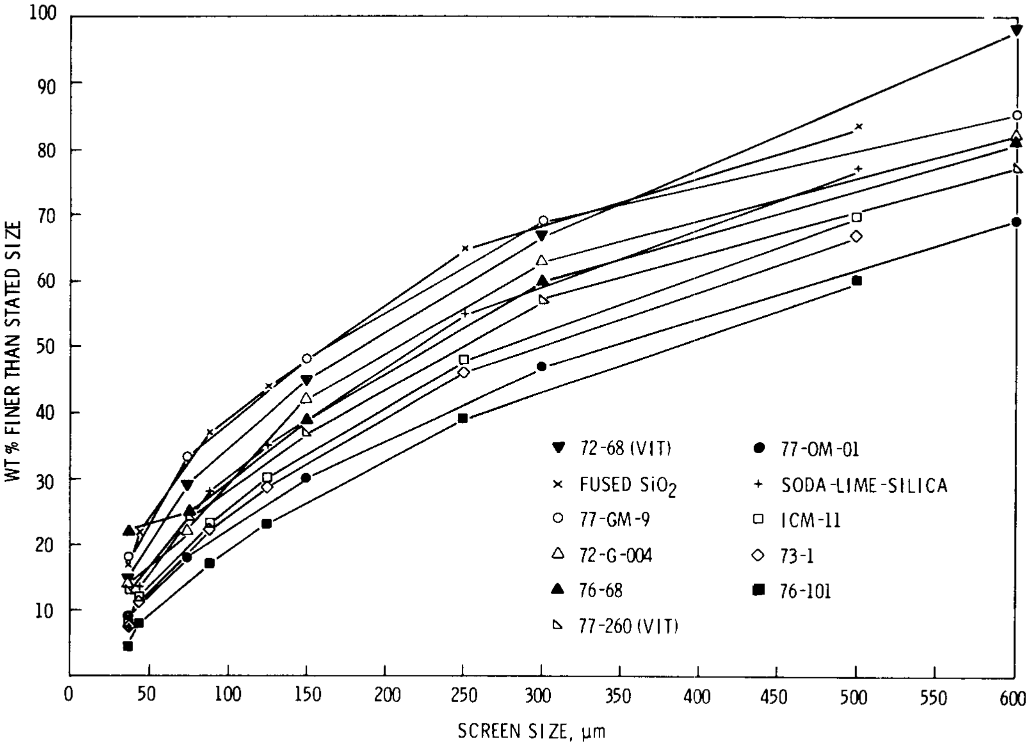

FIGURE 1. Sieve Size Analysis Results for a Wide Variety of Glasses, All Impacted as Identical Samples at an Energy of 216 Joules

It is common in glass science to correlate test results with glass composition-related factors such as the percentage of SiO_2 or the oxygen/silicon ratio. Good correlations exist in some glass systems with fundamental properties like density or elastic moduli. We attempted to make such a correlation with the impact data. The weight percentage of (-44 µm) fines was used as a *rough performance index*, and was plotted against either silica content or O/Si ratio. The resulting plots, included in Figures 2 and 3, show that no simple correlation exists.

In full-scale or part-scale impact tests conducted to date on glass-filled canisters, it is usually observed (Smith and Ross, 1975) that the severe damage is confined to the area of the impact itself, with little if any damage 1 m from the impact site.

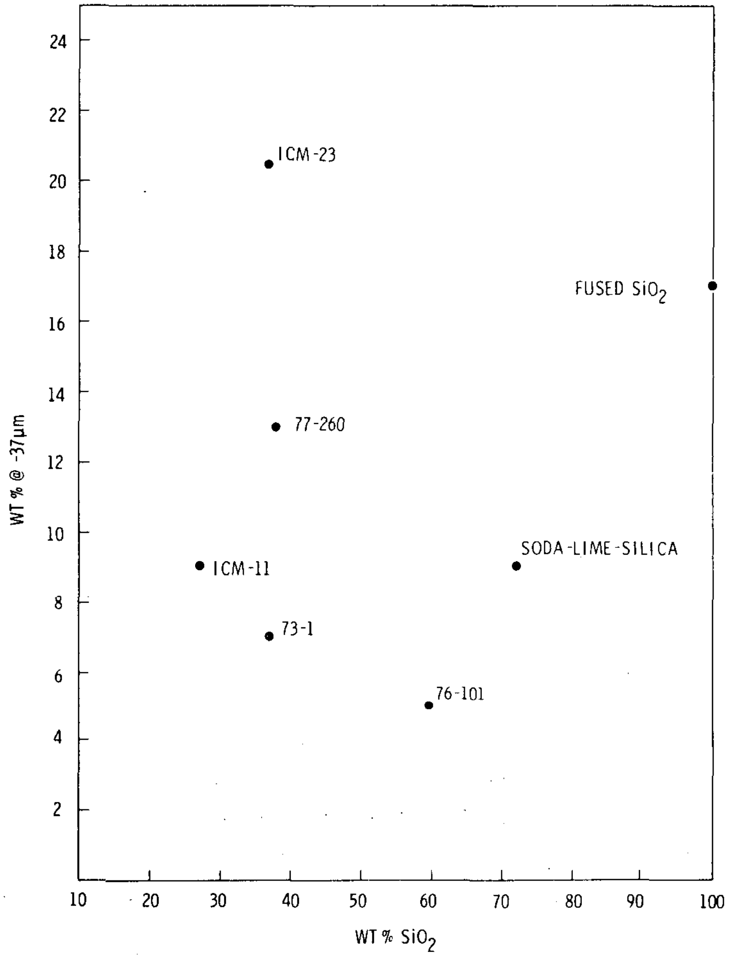

FIGURE 2. Percentage of (-44 µm) Fines Produced in a Variety of Glasses by a 217-J Impact Plotted Against the Percentage of SiO_2 in the Glasses

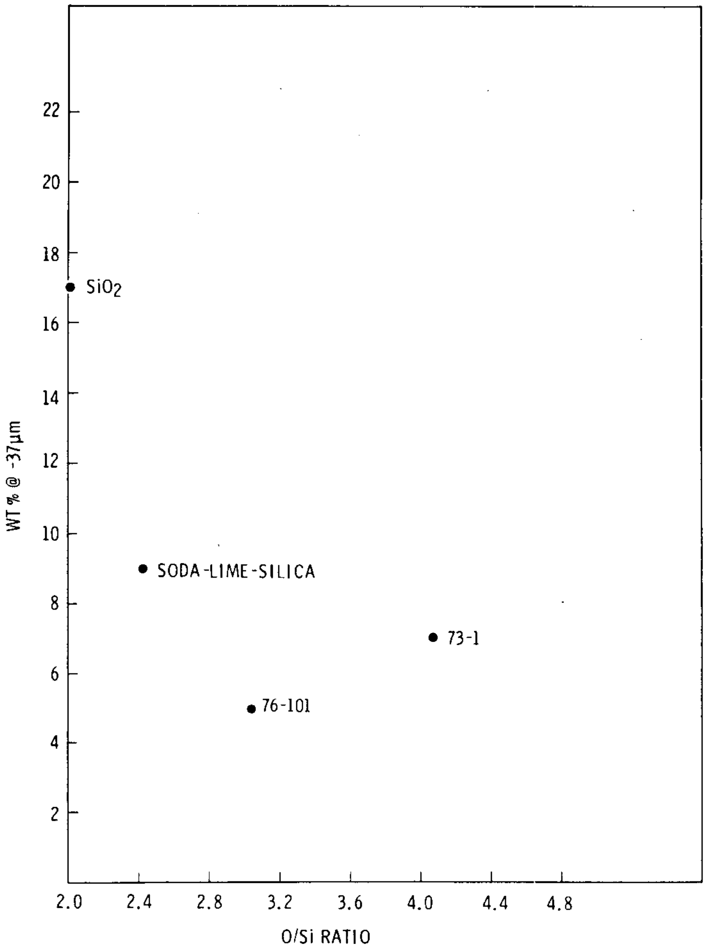

FIGURE 3. Percentage of (-44 μm) Fines Produced in a Variety of Glasses by a 217-J Impact Plotted Against the Corresponding O/Si Ratio for the Glasses

Canister KT-11 provides some data to the contrary, however. This 0.6-m-dia canister contained 1910 kg of glass and was dropped 7.6 m onto a concrete pad with no canister failure. Samples of the glass were taken at the immediate impact site and at a location 1.5 m away. The sieving results are plotted in Figure 4; note the log-log scales, which were necessary to represent all the data. The impact has produced substantial fine material; 1.08% of the impact zone sample mass was -44 μm, fifteen times the fraction (0.07%) produced at the further location. Figure 4 also shows that 50% of the glass at this further location is smaller than 5mm.

This degree of damage probably results from the structure produced by the slow-fill process using the continuous melter. This structure involves substantial amounts of poorly supported glass, which moves in response to the impact. Thus, although the elastic wave would not travel as well through the complex structure, the ability of the glass to move both at initial impact and during the 2 to 3 rebounds apparently produced a lot of secondary damage. We are trying to produce better can fills with lower porosity by means of canister insulation during heating. These treatments will also reduce the amount of peripheral thermal-shock cracking.

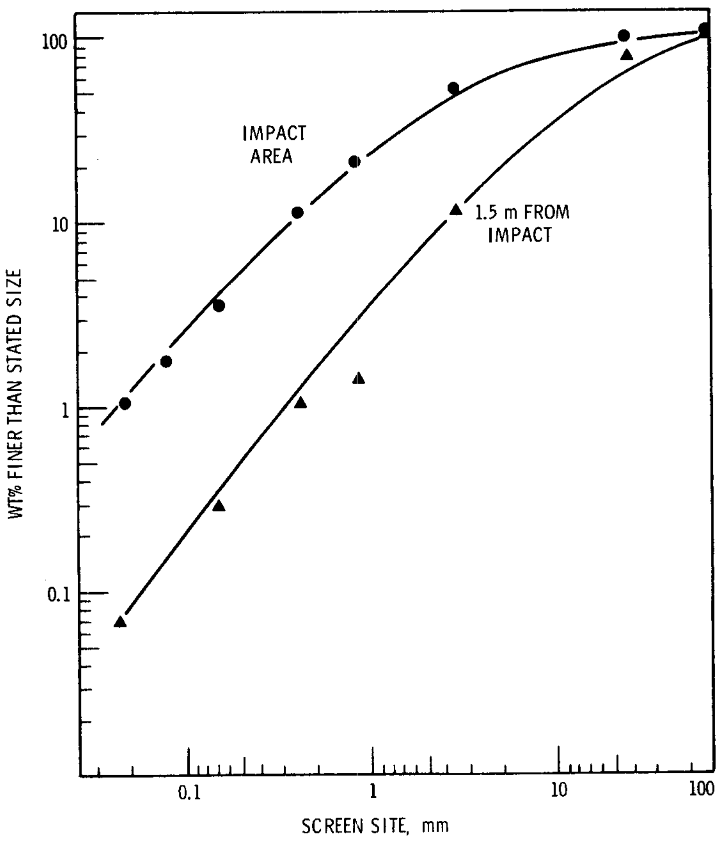

FIGURE 4. Sizing Data for Canister KT-11, Sampled in the Indicated Locations

SECTION 3 - ALTERNATIVE WASTE FIXATION PROCESSES

The goal of this task is to develop alternative waste fixation procedures that will serve as viable backup processes. Cost and safety factors of the alternative processes and products are to be compared to those of the current reference process and product--silicate glass castings in large metal canisters. These alternative processes are being developed on the laboratory scale. In the concept currently emphasized the waste is formed into small granules or pellets that are coated with nonradioactive, inert materials to provide containment and leach resistance. The coated waste shapes are then incorporated into a metal matrix that provides impact resistance and increased thermal conductivity.

COMPARATIVE STUDIES - R. O. Lokken, R. A. Wheeler, K. R. Welsch

Past attempts at comparing waste form properties have proven inaccurate, owing to discrepancies in testing conditions and methods. In the comparative studies program, ten waste forms will be tested and evaluated under identical conditions and procedures. The waste forms to be prepared and tested include:

- 76-68 simulated waste glass
- PW-9 calcine sintered-ceramic
- PW-9 calcine/frit sintered-ceramic
- cement containing 10 wt% PW-9 calcine
- cement containing 10 wt% SPC-5 supercalcine
- glass-ceramic containing 20 wt% PW-9 calcine
- hot-pressed PW-9 calcine
- hot-isostatic-pressed PW-9 calcine
- hot-isostatic-pressed SPC-5 supercalcine
- SPC-5 pellets in Al-12Si matrix
- simulated waste glass marbles in a lead alloy matrix.

The first ten waste forms will either be fabricated or core-drilled to a final size of ∿0.44 in. in dia by 0.50 in. high. The metal matrix waste forms will have a final size of 1.0 in. in dia by 1.0 in. high.

Evaluation of the waste forms will be based upon impact resistance, leachability, and volatility. The samples will be impacted with ∿160 ft-lb (1.7-J) impact energy. Following impact, the samples will be evaluated with respect to particle size distribution, percent fines (-37 μm) produced, and surface area increase. Leachability, often felt to be the most important characteristic of radioactive waste forms, will be determined by methods which deviate from the most common methods previously employed (Soxhlet and IAEA methods). The latter methods may result in leach rates that are misrepresentative of an as-fabricated waste form because of large surface areas. The method to be used in the comparative studies utilizes a bulk sample as opposed to powder. The samples will be exposed to distilled water for predetermined time and temperature. The leach solution will then be analyzed for specific ions that have been leached from the waste forms. This method is believed to represent a more realistic assessment of the effectiveness of radionuclide fixation in different waste forms.

To date, three waste forms have been prepared. One consists of 90 wt% Type II Portland Cement plus 10 wt% PW-9 calcine powder. The cement and calcine were blended dry to form a homogeneous mix. Distilled water was added and hand-mixed until a consistent paste was made. The paste was then cast into a mold 5 in. in dia by 1.75 in. high and vibrated to release any trapped air. The mold was sealed and the mixture allowed to set and harden for seven days. The second and third waste forms are sintered-ceramics--one consisting of 100% PW-9 calcine, the other made of 50 wt% calcine and 50 wt% glass frit. These samples were prepared by cold-pressing powder at a force of 2000 pounds. The "green" pellets were then sintered at 975°C and 750°C, respectively.

CARBON LEACH TESTING - W. J. Gray

Carbon is expected to have a very low leach 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.

Oxidation, rather than leaching, is probably a more accurate description of the mechanisms of carbon removal in aqueous systems. Nevertheless, the removal can be described in terms of g/cm^2-d and compared with the leach rates of other materials. Because the expected reaction products (CO and CO_2) are gases, leach testing must be done in a sealed vessel and, to be rigorous, samples of both the liquid and gas phases should be analyzed.

Recent tests have involved stirring distilled water and powdered graphite, whose surface area was 32 m^2/g, in a sealed vessel with air filling the space not occupied by water and graphite. Following each test, the stirrer was stopped and the reaction vessel was allowed to cool to room temperature and stand for one hour before a gas sample was extracted. The gas samples were analyzed with a gas chromatograph, and the amount of CO_2 found was always greater than CO by a factor of between 10 and 20. Both the CO_2 and CO were considered in computing the graphite reaction rate and, in addition, the concentration of CO_2 in the water was taken to be 80% of that in the gas phase. Thus, the reaction rate may be overestimated because the equilibrium concentration of CO_2 in water may not be reached only one hour after cooling. It was assumed that the water contained no CO. Finally, a blank run yielded 426 ppm CO_2 and 13 ppm CO; these values were subtracted from the results of the reaction tests. The blank CO_2 value agrees reasonably well with the amount ($\sim$300 ppm) in a standard air sample. Reaction rate results are shown in Figures 5 and 6.

Figure 5 shows that the reaction rate decreases with time. This implies either that some product is formed which somehow interferes with the reaction mechanism, thereby decreasing the rate, or that an approach to equilibrium is taking place. The latter seems more likely.

Figure 6 shows an Arrhenius plot of 24-hr tests. A more rigorous treatment would show initial reaction rates rather than rates averaged over 24 hours. Not enough data are yet available to determine initial reaction rates, however.

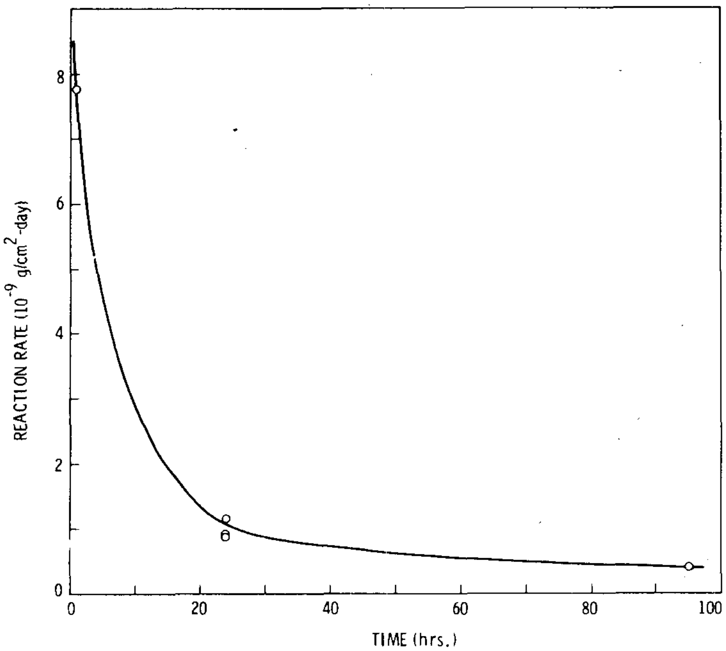

FIGURE 5. Reaction Rate of Graphite Powder in Distilled Water at 95°C

The slope of the Arrhenius plot in Figure 6 gives an activation energy for the reaction of about 9 kcal/mole. Yet the enthalpy for the reaction

$$C + 2H_2O(l) \rightarrow CO_2(g) + 2H_2(g)$$

is 42 kcal/mole at 20°C and, because it is endothermic, the activation energy must be at least that large. The very low activation energy measured, therefore, suggests that the carbon is reacting with something other than water--probably with dissolved oxygen. We have begun efforts to measure the reaction rates in an oxygen-free vessel.

The reader is cautioned that the absolute values of the reaction rates that are shown in Figures 5 and 6 are very uncertain, primarily because it is not yet known just what reaction has been measured.

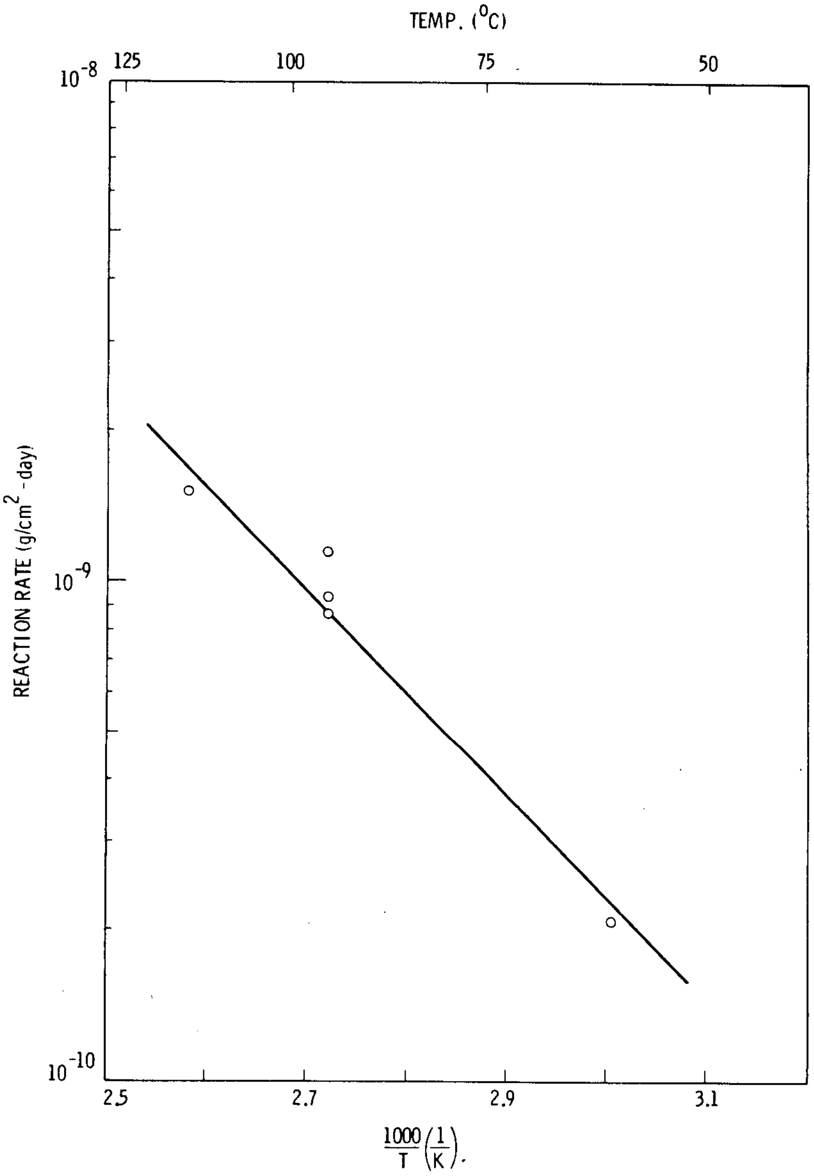

FIGURE 6. Reaction Rate of Graphite Powder in Distilled Water Averaged over 24 hr

GEOLOGIC MATERIALS: IMPLICATIONS FOR RADIOACTIVE WASTE DISPOSAL - R. C. Ewing and R. F. Haaker

A preliminary draft of a report on the long-term stability of natural analogues to crystalline (e.g., supercalcine) waste forms has been completed. The report details mineralogic, structural, geochemical, occurrence, age, alteration and radiation damage data for ten relevant natural phases. Conclusions of this report include:

- If transuranium elements are not present in the primary phase, then α-particle damage that produces large volume changes or metamictization of phases such as apatite, uraninite or monazite should not be of importance in the time scale of concern (10^5-10^6 yr).
- If transuranium elements are concentrated, some phases, such as apatite, will become metamict within a period of years to thousands of years. A large volume increase is certain to accompany the transition of apatite to the metamict state. By analogy with $^{238}PuO_2$, the uraninite phase will not become metamict but may become one or two percent less dense as a result of radiation damage. The behavior of the monazite phase cannot be predicted from the available data.
- Rapid loss of ^{137}Cs from pollucite and alteration of both pollucite and nepheline to clays with a large increase in volume may occur at the most extreme repository conditions, which have been postulated to be hydrothermal brine at 200^o to 400^oC.
- Under ideal conditions, the natural analogues to many of the supercalcine phases persist in substantially unaltered form for periods of time in excess of 10^9 years.

During the next quarter, radiation damage experiments on the $ThSiO_4$ dimorphs, thorite and huttonite, are scheduled to begin in collaboration with PNL investigators.

REFERENCES

McElroy, J.L., J.E. Mendel, W.F. Bonner and M.H. Henry. 1979. Quarterly Progress Report - Research and Development Activities - High-Level Waste Immobilization Program: January Through March 1978. PNL-2999-1. Pacific Northwest Laboratory, Richland, WA 99352

McElroy, et al. 1979. Quarterly Progress Report - Research and Development Activities Waste Fixation Program - October Through December 1977. PNL-2265-4, Pacific Northwest Laboratory, Richland, WA 99352.

Slate, S. C., et al. 1978. Stresses and Cracking in High-Level Waste Glass. PNL-SA-7369, Pacific Northwest Laboratory, Richland, WA 99352.

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