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October through December 1976

by
J. L. McElroy

November 1977

Prepared for the
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Battelle

Pacific Northwest Laboratories

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QUARTERLY PROGRESS REPORT
RESEARCH AND DEVELOPMENT ACTIVITIES
WASTE FIXATION PROGRAM
OCTOBER THROUGH DECEMBER 1976

by
J. L. McElroy

November 1977

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Richland, Washington 99352

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PREVIOUS REPORTS

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

PREVIOUS WORK

This project reports on the development of a system for processing
research and development activities in a reactive manner. Previous
projects reported have been 1995, 1996, 1997, 1998, 1999, 2000, 2001, 2002,
2003, 2004, 2005, 2006, 2007, 2008, 2009, 2010, 2011, 2012,
and 2013.

SUMMARY

Research and development activities of the Waste Fixation Program for October through December 1976 are described in this report. The objective of this program is to develop processes to convert high-level radioactive liquid waste (HLLW) to solid forms that are demonstrated to be physically, chemically, and radiolytically stable and inert. The scope of this program encompasses plans to make available a flexible advancing technology for the solidification of radioactive waste. Early technology will produce borosilicate glass by in-can melting and continuous electric melters. Multibarrier waste forms will be developed for future application.

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

- An engineering-scale in-can melting (ICM) run was made that confirmed a melting rate of 48 kg/hr in a 12-in.-diameter canister containing a drop-in fin assembly consisting of 8 fins.
- The feasibility of accurately monitoring the melt level was demonstrated, using equipment located outside the cell. The interface can be located to within 1 in.
- Increased emphasis has been placed on canister design and development. The program, which will lead to a final selection of a canister design, includes material evaluation, heat transfer analysis, strength analysis, and closure design.
- Long-term (5 year) thermal effects studies began on a low-zinc waste glass formulation. Initial results indicate that this formulation has greatly improved devitrification properties.
- Development of several options for multibarrier waste forms continued.

 

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QUARTERLY PROGRESS REPORT
RESEARCH AND DEVELOPMENT ACTIVITIES
WASTE FIXATION PROGRAM
OCTOBER THROUGH DECEMBER 1976

INTRODUCTION

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

The research and development activities in radioactive waste fixation for the reporting period of October through December 1976 are described in this report.

SECTION 1 - WASTE FIXATION PROCESS DEVELOPMENT

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

IN-CAN MELTING (H. T. Blair)

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

An engineering-scale in-can melting (ICM) run was made that sustained a 48-kg/hr melting rate for 3 hr in a 12-in.-diameter can containing a drop-in fin assembly consisting of 8 radial fins; both the can and fins were made from 304L stainless steel.

The run demonstrated the use of a gravimetric feeder to meter a blend of frit and spray-dried calcine at an overall frit-to-calcine ratio of 2.4:1. The run also demonstrated the use of an airlock to admit the batch into the process envelope and the use of SiC as an additive to the batch to both prevent the formation of soluble molybdates and to serve as a fining agent.

MELT LEVEL AND RADIONUCLIDE DEPOSITION MONITORING BY GAMMA EMISSION

(W. F. Bonner and R. L. Brodzinski)

The feasibility of accurately monitoring the melt level using equipment located outside the cell was demonstrated. This technique involves monitoring the gamma emission of specific isotopes in the waste. A series of small holes in the cell wall is used for collimation. These holes need not penetrate the stainless steel cell liner.

Testing to date, using glass-filled high-level waste (HLW) canisters prepared during the Waste Solidification Engineering Prototype (WSEP) program, shows that the waste/air interface can be located to less than 1 in. (2.5 cm)

and that nonhomogeneities within the glass can be observed as long as the total line-of-sight bulk density is less than 50 g/cm^2 .

This technique can also be used to detect deposition of radionuclides in any part of the solidification equipment. Any such buildup can be monitored and remedial measures initiated before operational problems occur. Because it is possible to differentiate between isotopes, it is expected that selective depositions of elements such as ruthenium and other semivolatile species can also be monitored by this technique.

SPRAY CALCINER DEVELOPMENT (L. S. Romero)

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

Several runs were conducted to obtain additional information on ruthenium and to support ICM studies. The spray calciner produced 130 lb of calcine in 16 hr without any operational or maintenance problems.

Ruthenium balance on a full-level nonradioactive ruthenium run shows that ruthenium is in the nondetectable range in the off gas and that no plating out of ruthenium is occurring in the spray calciner unit.

OFF-GAS SYSTEMS (M. S. Hanson)

The purpose of this work is to generate information to be used in the design and selection of waste solidification off-gas control systems.

Construction of a common off-gas system to be used by all nonradioactive calciners and melters in the nonradioactive engineering development laboratory is nearing completion. The system design incorporates previous reprocessor feedback. The off-gas train consists of a venturi scrubber, a tube and shell condenser, a packed scrub column and a HEPA filter. Provisions were made for future installation of fission-product adsorption beds and nitrogen-oxide control devices. The system is of high capacity and will be operable in the next reporting period.

FLUIDIZED-BED CALCINATION (W. J. Bjorklund and J. C. Hartl)

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

Scoping runs with the fluidized-bed calciner have continued this period. Highlights of the operation are:

- The conical type distributor plate, which replaced the flat perforated plate, has functioned extremely well.
- Successful use of the tube type feed nozzle continued.
- Operation with the feed nozzle spraying through the flame of the fuel nozzle resulted in erratic fuel nozzle behavior.

Several short runs have been made using the calciner off gas as a heat load for testing a packed quench scrubber.

Future plans include:

- installing an additional off-gas system in the development laboratory consisting of a series of venturi scrubbers, steam jet and water eductor condenser;
- installing an air lift feed system;
- testing commercial fuel nozzles for combustion or preheating service;
- beginning preliminary designs for coupling the existing fluidized-bed calciner directly with a continuous ceramic melter. A new melter will be built for this service. Scheduled completion is near the end of CY-1977. A layout of a proposed coupled system is shown in Figure 1.

FIGURE 1. Fluidized-Bed Ceramic Melter Vitrification System

JOULE-HEATED CERAMIC MELTER (C. C. Chapman)

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

The scale-model ceramic melter has continued to idle at operating temperature. The refractories and power electrodes have been exposed to the molten glass for 22 months. This unit will be shut down during the next quarter for corrosion assessment. One experiment with this unit suggests that volatility during nonproduction periods can be successfully controlled by reducing the power to the melter. This produces a cool top surface, which serves as a barrier for volatile species. This melter operated with stability at a low power level.

The major effort has been to complete the direct-liquid-fed ceramic melter. Installation is progressing and the system should start up early next quarter.

Development of a hydrodynamic heat transfer computer model for the joule-heated ceramic melter has begun. After this code is developed, it will be used to assess various proposed designs and should provide better understanding of system operation.

CANISTER DEVELOPMENT PROGRAM (S. C. Slate)

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

HLW canisters are being developed for use in the ICM and continuous melter solidification processes. The program includes: material evaluation, heat transfer analysis, strength analysis, closure design, and canister design. A test program is included to verify analyses and to evaluate design performance. This extensive development program has been established because the canister design must be closely coupled to the design of the solidification equipment. Work in these areas is summarized below.

Canister design effort has been directed primarily towards canisters to be used in the ICM process and then stored in a water basin for up to 10 years.

We have assumed that no overpack will be used until shipping and have ignored establishing a firm diameter or length. Our work has been on designs of the top and bottom of the canister and methods to reduce wall stress and control corrosion. Canisters are presently being designed for our new full-scale solidification equipment, and fabrication techniques and the effects of safety and handling requirements on our designs are being evaluated.

Areas of concern for material evaluation have been corrosion and high-temperature strength properties of materials. Three main modes of corrosion on canisters have been studied:

- canister oxidation by air during processing,
- attack from the melt and melt vapors during processing, and
- corrosion during interim water basin storage.

From this research it is concluded that corrosion by these modes on stainless steel canisters used in the ICM process is insignificant or can be controlled.⁽¹⁾

To identify high-temperature (1100°C) properties, estimates were made from tests performed at lower temperatures. Strength and creep properties of Inconel 601 and 304L SS have been estimated and creep tests of these materials in the range of 950 to 1150°C are being run. The results from this work will be available soon.

Heat transfer work has been aimed at modeling canisters with different diameters and heat loads in a variety of environments. Results in this area have been reported previously.⁽²⁾ We are presently involved in measuring glass conductivity and developing a dynamic model of the glass.

To evaluate different canister designs, three commercial computer codes have been adapted to model the canister. Modeling of the canister during ICM processing has provided very useful design data. Significant material reductions and design simplifications can be made by supporting the canister from the bottom. High stress areas in the canister have also been identified and changes in the design made to eliminate them. Empirical data from actual canisters is now being correlated to verify the models. To date the models have been shown to approximate the measured data.

A canister closure is now being designed for plant application and will include performance criteria from regulating agencies. This system includes the canister lid, an overpack and its lid, a welder, and inspection techniques and equipment. Prototypical equipment is expected to be built by the middle of 1977.

Efforts to reduce residual stresses in the canister wall have been partially successful. This reduction is desirable from the standpoint of decreasing the possibility of stress corrosion cracking in the water basin. It has been demonstrated that liners inside the canister are able to reduce stress levels by 90%. However, these liners are subject to attack from the melt and they inhibit heat transfer. Quenching the canister in water from 800°C can also reduce stress by 50%. Other corrosion control techniques are discussed in Reference 1.

Decontamination of the canisters is also being studied. A water spray system has been evaluated. Currently, the use of electropolishing techniques to decontaminate the canister are being evaluated. Results indicate that this method will remove heavy oxide and contamination from the canister.

The goal of the canister development program is to meet the requirements of both the waste processors and the regulating agencies. These requirements should be combined into a prototypical design for a solidified HLW canister by 1978.

SECTION 2 - WASTE FORM CHARACTERIZATION

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

MELT DEVELOPMENT (W. A. Ross)

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

The main effort this quarter was to develop a melt formulation suitable for "clean" waste processing in the ceramic melter. Reducing agents for molybdate control are undesirable in the ceramic melter, therefore the major development efforts are being directed to molybdate control by modifications of the glass compositions. The important variables for a fixed waste content that have been identified include Na_2O content, K_2O content, B_2O_3 content and melting temperature.

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

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

Glass 76-68 is undergoing thermal treatment according to the temperature-storage time matrix shown in Table 1. PW-8a-3 calcine and 76-101 frit were melted together at 1050°C to form the glass. Table 2 shows the nominal compositions of PW-8a-3 and 76-68 glass. After thermal treatment the glass samples will be examined for density, leachability and phase behavior.

TABLE 1. Storage Conditions for Thermal Effects on Stored Glass Study

<u>Temperature, °C</u>	<u>Time</u>				
	<u>2 Hours</u>	<u>1 Day</u>	<u>1 Week</u>	<u>2 Months</u>	<u>1 Year</u> <u>5 Years</u>
1200	X				
1100	X				
1050	X				
1000	X				
900		X	X	X	
850		X	X	X	
800		X	X	X	
750		X	X	X	X
700		X	X	X	X
650		X	X	X	X
600		X	X	X	X
550		X	X	X	X
500		X	X	X	X X
400				X	X X
300				X	X X

TABLE 2. Composition of PW-8a-3 Calcine and 76-68 Glass

PW-8a-3 Molarity at 378 ℓ /MTU		76:68 [PW-8a-3(1:2)76-101] Glass, wt% ✓
0.010	Rb	0.13 Rb ₂ O
0.027	Sr	0.38 SrO
0.014	Y	0.21 Y ₂ O ₃
0.106	Zr	1.77 ZrO ₂
0.117	Mo	2.28 MoO ₃
0.059	Ru	1.07 RuO ₂
0.010	Rh	0.17 Rh ₂ O ₃
0.032	Pd	0.53 PdO
0.002	Ag	0.03 Ag ₂ O
0.002	Cd	0.03 CdO
0.012	Te	0.26 TeO ₂
0.054	Cs	1.03 Cs ₂ O
0.027	Ba	0.56 BaO
0.024	La	0.53 La ₂ O ₃
0.051	Ce	1.19 CeO ₂
0.023	Pr	0.53 Pr ₆ O ₁₁
0.0732	Nd	1.67 Nd ₂ O ₃
0.014	Sm	0.33 Sm ₂ O ₃
0.003	Eu	0.07 Eu ₂ O ₃
0.002	Gd	0.05 Gd ₂ O ₃
0.1202	U	4.58 U ₃ O ₈
0.902	Fe	9.77 Fe ₂ O ₃
0.040	Cr	0.41 Cr ₂ O ₃
0.020	Ni	0.20 NiO
0.050	PO ₄	0.48 P ₂ O ₅
1.200	Na	12.51 Na ₂ O
		39.80 SiO ₂
		9.47 B ₂ O ₃
		2.00 CaO
		4.97 ZnO
		2.97 TiO ₂

THERMAL AND MECHANICAL SHOCK (L. R. Bunnell)

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

A large amount of data has been collected on the impact fracture of soda-lime-silica (plate) glass. BET surface area data seem to indicate a roughly linear correlation between impact energy and surface area. Similar data have been collected for devitrified and vitreous Corning glass, for fused silica, and for a frit (73-1) of interest to the waste program.

To lay a foundation for later comparisons, a common glass of relatively fixed composition (soda-lime-silica plate glass) is being used. The glass specimens are 0.440 in. in diameter by 0.50 in. high and are right cylinders produced by core drilling. The size and shaping technique is judged appropriate for the specimens that will eventually be taken from full-scale canisters. The specimens are placed in a hardened, oversized die as shown in Figure 2, and the punch is impacted by a falling weight. The punch in Figure 2 includes swirl chambers, which reduce the amount of glass ejected from the die by the pumping action of the punch. This material originally amounted to ~2%, but losses have been cut to ~0.4% by the swirl chambers.

After crushing the glass with a known amount of energy, the pieces are sized by sieve analysis, usually to a minimum of 37 μm . Sieves for 30, 20, 10, and 5 μm are available and have been used in some cases. BET surface area analysis has also been performed and the results compared with the energy input in an attempt to relate the two.

Figure 3 shows the present data on plate glass and indicates size distribution as a function of impact energy. All of the curves represent the average of several impacts, and points from several tests are included to show scatter. The principal effect of higher energies is to increase the fraction of fines because the curves are displaced in a nearly parallel manner as energy increases.

FIGURE 2. Punch and Die Arrangement Used for Impacting Glass Specimens. The bore is 1.0 in. to allow a free collapse of the sample. (A), (B) and (C) show the evolution of the present design and the swirl chambers.

FIGURE 3. Averaged Size Distribution Curves for Soda-Lime-Silica Glass Impacted at Four Different Energies

An impact test using multiple impacts has been described by Wallace and Kelley.⁽³⁾ The use of multiple impacts seemed somewhat unrealistic in terms of an accident situation; furthermore, our work shows that the particle-size distribution is a rather strong function of the number of impacts. Figure 4 shows particle sizes produced in soda-lime-silica glass by the same total amount of energy (158.4 ft-lb) applied as a single impact or in up to eight impacts. In the multiple impacts, the particles were stirred after each impact to randomize them. A large difference exists between single and multiple impacts, particularly in comparing one, two, and three impacts. At greater numbers of impacts, the bed of particles probably distributes the energy so that point loading effects decrease. It is thus advisable to use

an impact machine that can deliver high energies at one blow. Since the eight-impact specimens contained ~25 wt% of $-37\ \mu\text{m}$ particles, a special analysis was made that indicated that the $-10\ \mu\text{m}$ fraction is about 4%. In this particle size range, static charge effects can dominate, so a more thorough examination of the fines fractions will be done by a settling technique, which should be less subject to charging effects.

FIGURE 4. Size Distribution for Soda-Lime-Silica Glass Impacted by the Same Total Amount of Energy, 158.4 ft-lb, Applied as Single or Multiple Blows

The BET surface area of the impacted soda-lime-silica glass was determined as a function of impact energy, and the results are shown in Figure 5. Also included in the figure is a single data point for 73-1 frit containing no additives. The results show a roughly linear relationship of surface area to impact energy for plate glass. It would be convenient for accident analysis if this relationship held for glasses containing waste. Division of surface area by impact energy produced an average value of $2.9 \times 10^{-3} \text{ m}^2/\text{joule}$. A value of 3.85 joule/m^2 is given in the literature⁽⁴⁾ for the surface energy of soda-lime-silica glass, which corresponds to $2.6 \times 10^{-1} \text{ m}^2/\text{joule}$. As would probably be expected, the impact process is complex enough so that only ~1% of the available energy is used in creating new surface area.

FIGURE 5. BET Surface Area for Impacted Soda-Lime-Silica Glass as a Function of Impact Energy

Fused silica and frit 73-1 containing no calcine were also impacted; the former to serve as baseline data and the latter as a step in the approach to actual ICM glass. Figure 6 shows the results for the three glasses (plate glass, fused silica, and frit 73-1) at four different impact energies. The fused silica is the most severely fragmented, with ~84% less than 500 μm at 158 ft-lb. The 73-1 frit, on the other hand, has only 66% <500 μm particles at this energy level. The plate glass is midway between these two and, at the lower impact energies, the ranking remains consistent. The reason for this particular stacking order is not clear at present, but it is noteworthy that the impact resistance seems to be increasing with the amount of added materials dissolved in the glass.

FIGURE 6. Comparison of Size Distribution for Three Different Glass Types (Plate, Fused Silica, and 73-1 Frit) at Four Different Impact Energies

WASTE VAPORIZATION STUDIES (W. J. Gray)

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

Table 3 lists compositions of glasses being studied to test a hypothesis that TiO_2 additions reduce cesium volatility. Gross weight-loss data obtained to date for these glasses are shown in Figure 7. The absolute weight-loss difference between a glass with no TiO_2 and one with 3% TiO_2 probably is not significant, but the difference in the shapes of the curves for glasses with and without TiO_2 may be significant in that they may indicate different vaporization mechanisms. Concentrations of TiO_2 greater than 3% cause increases in the gross weight loss. Vapors have been collected and are currently being analyzed to determine the effects of TiO_2 additions on vapor composition.

TABLE 3. Glass Composition

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

FIGURE 7. Weight Loss in Dry Air at 1100°C

STANDARD TESTS DEVELOPMENT (J. M. Rusin)

The purpose of this work is to develop standard tests for intra-and inter-laboratory comparisons of waste form properties for potential use by the regulatory agency to demonstrate conformance to established standards.

Impact-Leachability Test

To combine a leaching and impact test, a suitable material must be found to contain the fine particles produced upon impact. Present efforts have been directed to a polycarbonate filter medium, Nuclepore. Sheets of Nuclepore filters can be obtained down to pore sizes of 0.05 μm . The material can be easily cut and bags formed by heat sealing. The material has excellent resistance to acid but can only tolerate weak bases.

Several tests have been run on alumina beads and ground glasses. The bags containing alumina beads are unaffected during a standard 72-hr Soxhlet test. Some of the bags containing ground glasses split or ruptured during the Soxhlet test. A few have been lost to faulty seals, which can be corrected with experience. Further tests will be conducted on the Nuclepore material and alternate materials will be acquired for testing.

As part of the combined impact-leachability test, standard Soxhlet leach tests were run on four typical glasses that are part of the impact study. The results are listed in Table 4. Surface area determinations were made on the samples before and after leaching; the results are listed in Table 5. A relationship appears to exist between the Soxhlet weight loss and increased surface area on the leached sample. This is especially evident with the plate glass sample where the 22% Soxhlet weight loss corresponds to an increase in surface area of two orders of magnitude.

TABLE 4. Standard Soxhlet Leach Test Results

<u>Sample</u>	<u>wt%(a)</u>
909IQY Devitrified	0.50
909IQY Vitreous	0.59
Plate Glass	22.00
ICM-11	0.35

(a) -42+60 mesh sample for
72 hours.

TABLE 5. Surface Area Determinations Before and After Leaching

<u>Sample</u>	<u>As Fractured Surface Area (m²/g)</u>	<u>Leached Surface Area (m²/g)</u>
909IQY Devitrified	0.0250	0.0490
909IQY Vitreous	0.0280	0.0680
Plate Glass	0.0360	3.7000
ICM-11	0.0260	0.1150

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

The purpose of this task is to characterize the glasses produced on an engineering scale by the Nuclear Waste Processing Section.

Two engineering-scale in-can melts (ICM-16 and 18) have been selected for detailed characterization. The properties that are important for disposal considerations will be measured. Particular attention will be given to chemical segregation and its effects on leachability, density, thermal conductivity, and thermal expansion. ICM-16 is a 12-in.-finned can with PW-7a-2(1:2) 75-75 +1.5 wt% silicon glass. ICM-18 is an 8-in. can with PW-8a-2(1:2) 75-75 +1.5 wt% silicon glass. Future engineering melts with different glass compositions will also be characterized.

FULL-LEVEL RADIOACTIVE TESTS: C-CELL GLASS MAKER (Y. B. Katayama)

Fully radioactive waste glass specimens are being prepared on a laboratory scale. The gases evolved during melting of the radioactive glass are being analyzed.

Glass batch number CW-11 was heated from ambient temperature to 1050°C in 5 hours. The melt was held at 1050°C for 6 hours before furnace cooling. The platinum chill plate collected 0.0920 g of condensable volatilization product during the glass forming process. This condensed product was 6.5 times greater than that collected during run CW-6 where the heatup time was 70 min.

Radiochemical analysis of the off-gas scrubber solutions, for prior runs, has shown nearly equal ^{137}Cs concentrations in the caustic scrubber and water scrubber. This high analysis in the final scrubber indicates incomplete removal of the ^{137}Cs from the off-gas stream. In run CW-11, a nitric acid scrubber was put into the head-end of the off-gas treatment stream. Gamma scan analysis of the scrubber solutions indicated that 94.5% of the ^{137}Cs accountable in the noncondensable off-gas stream was trapped in the nitric acid scrubber.

FULL-LEVEL RADIOACTIVE GLASS CHARACTERIZATION (D. J. Bradley)

Characteristics of fully radioactive glass specimens must be compared with nonradioactive glasses of similar chemical composition as a function of storage conditions to validate the voluminous data which have been obtained on nonradioactive glasses.

A second series of leach solutions has been analyzed by gamma spectroscopy and is the result of 7 months of leaching high-level waste glass wafers in deionized water. These solutions are currently undergoing a cesium removal operation after which they will be gamma counted again and analyzed for beta and alpha emitters. To estimate the initial activity in the glass wafers, a sample of the HLW calcine has been dissolved and is also currently being analyzed for alpha, beta, and gamma emitters.

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

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

During this quarter, a major effort was directed toward completing the full-level waste glass (72-68) examination at the Battelle Columbus Laboratory's (BCL) West Jefferson hot lab facility. Work has also continued onsite to further characterize the Nuclear Fuel Services (NFS) type glass composition 76-68.

Full-level waste glass samples at BCL's West Jefferson facility were examined through the combined use of optical metallography and shielded electron microprobe analysis. Microprobe examination has indicated significant compositional differences between the "hot" samples and the cold reference glass 72-68. The general appearance of the active samples, however, resembled typical inactive samples, with a mixture of glassy regions and undissolved agglomerated regions evident. Another important result from this study, obtained from counting statistics, indicated that the shielded microprobe method appears capable of elemental analyses for full-level waste glasses with reliability comparable to work on inactive samples.

Using a standard slow-cool rate from the preparation temperature designed to produce maximum crystal yield, a devitrified sample of 76-68 glass was prepared. Examination of both vitreous and devitrified samples indicates overall crystal sizes $<10\text{ }\mu\text{m}$. Ruthenium, palladium, and chromium were found to be the primary contributors to the undissolved phases present. With respect to devitrification, this glass composition is probably as good as can be hoped for. The compounds formed are refractory, radiation damage resistant, simple oxides, and the crystals are quite small.

A new area of work has begun during the past quarter dealing with ion bombardment studies on the glass compositions developed. The objective will be to establish the level of radiation damage required to cause serious property changes and to ascertain whether the technique can be used to complement the current ^{244}Cm doping work.

SECTION 3 - ALTERNATIVE WASTE FIXATION PROCESSES

The goal of this task is to develop alternative waste fixation processes and evaluate their waste form products to assure that viable backup processes will be available if needed. The alternative processes and products are to be compared for cost and safety to the current reference process and product, silicate glass castings in large metal canisters. The alternative processes are being developed on the laboratory scale.

GLASS MARBLE DEVELOPMENT (J. M. Rusin)

The purpose of this work is to develop methods to produce waste glass marbles in remote facilities and to evaluate glass-metal matrix reactions.

Three glass marble manufacturers were visited to: 1) survey possible marble production methods, and 2) obtain a supplier of small lots (<1 ton) of simulated HLW glass marbles for demonstration purposes. Two of the companies, Peltier Glass and Gladding-Vitro, manufactured marbles by the conventional method of gobbing into grooved rolls. The third company, Corning Glass Works, used a patented technique incorporating vibrated graphite molds and a continuous glass stream. For purposes of capacity and remote adaptability, the latter method is best suited for the Multibarrier Development Task. All three companies indicated that they could produce sample marbles.

As-received samples of 72-68 glass marbles conventionally cast in a Pb-10Sn matrix have been polished and characterized. There is a 30- to 50- μ m gap between the marbles and the matrix. No evidence of a reaction between the glass and lead exists. Previous matrixes of pure lead demonstrated a narrow reaction zone between the lead and glass. In general, there were considerable porosity and unfilled regions around the marbles. Vacuum casting is being pursued to correct these problems.

Additional samples of 72-68 glass marbles in Pb-10Sn matrix have been heat treated at 200, 300, 400, and 500°C for 10 days. Since the alloy melts

near 280°C, all but the 200°C samples were contained in alumina (AD998) crucibles. The top of the crucible was sealed with castable cement (Ceramacast 505) to prevent the marbles from floating to the top. A small vent hole was provided for vapor release. Except for surface lead oxidation no apparent reactions between the marbles and matrix can be visually observed. Micrographs of sectioned samples will be obtained.

DISC PELLETIZER EVALUATION (A. A. Garrett)

The disc pelletizer is being evaluated to determine if: 1) it can be used to make high quality spherical cores (pellets) from supercalcine; and 2) if it can be used to coat the above cores with glass frit. This process also involves sintering the bare cores and the coatings, placing the coated cores in a metal canister, and filling the canister with a metal matrix material.

During this quarter, full-scale (5 MTU/day) disc pelletizer production of high quality spherical cores (pellets) was demonstrated in three different 1-hour runs. Thirty-five kilograms of 0.5- to 8-mm-diameter supercalcine (SPC-2)⁽²⁾ cores were produced. A small weight percent of dry clay binder mixed with the SPC-2 powder before pelletizing produced cores with green strengths superior to those without clay binder.

Several batches of these cores were successfully coated in a pelletizer using various types of frit. The unfired frit coating appeared quite satisfactory; however, when fired, a thermal expansion mismatch between the coating and the core caused the coating to crack. Expansion matching tests are being performed to correct this problem.

CVD COATING DEVELOPMENT (M. F. Browning)

The purpose of this study is to develop coating materials and processes that can be applied to waste particles to serve as a fission product barrier. Current efforts are being directed toward duplex, $\text{PyC}/\text{Al}_2\text{O}_3$ coatings on 1- to 10-mm pellets.

During the current quarter the major effort has continued to be the application of a duplex (Al_2O_3 over PyC) coating on spherical simulated supercalcine waste particles (1 to 2 mm in size). Also, the use of a drum in place of the fluidized-bed technique for applying the desired coatings was further considered. Characterization of Al_2O_3 coatings, which were applied at three different temperatures from aluminum chloride and one temperature from a nonhalide precursor, aluminum ethylate, also continued.

As indicated in previous reports, crack-free Al_2O_3 and PyC coatings have been satisfactorily applied individually to supercalcined particles, but Al_2O_3 coatings applied over PyC on the same substrate resulted in a portion of the coated particles having cracked Al_2O_3 coatings. The initial hypothesis, that thin cracking is due to a thermal expansion mismatch between the Al_2O_3 coating and the PyC/calced waste substrate continues to be the most likely hypothesis. Alumina was satisfactorily applied to supercalcined waste because the friability of the waste accommodated the expansion mismatch. However, the PyC coatings infiltrated the porous structure of the waste particles, which strengthened them, reducing their friability and their ability to offset the expansion differences. Crack-free PyC coatings were obtained because their thermal expansions ($6 \times 10^{-6}/^\circ\text{C}$) more closely match that of the waste particles and/or they were more able to accommodate expansion differences because of their greater elasticity as compared to that of Al_2O_3 .

Two basic approaches to overcoming the cracking problem are under investigation. Both involve using a relatively weak crushable material to accommodate the expansion mismatch. An Al_2O_3 coating applied at $\sim 900^\circ\text{C}$ typically has a porous structure with a density of only $\sim 2.5 \text{ g/cm}^3$ (3.9 g/cm^3 for dense Al_2O_3), which can, potentially, provide a crushable layer between the PyC waste substrate and the dense impervious outer Al_2O_3 coating. A PyC coating applied so as to give roughly a 50% dense material might also be used as the crushable layer, but these coatings are usually applied at temperatures above 1300°C ; this is above that which the current supercalcined waste can readily tolerate. The second approach is to preserve the inherent crushability of the supercalcined waste particles during the PyC coating operation.

In most of the duplex coating experiments made this quarter a spherical supercalcined waste, fired at 1100°C, with a particle size of 1 to 2 mm (SPC-2) was used with a fluidized-bed system in which a bed diluent of ZrO_2 (420 to 707 μm) particles was used with the waste to facilitate particle movement. In applying PyC coatings, a diluent/waste ratio of 2:3 was used; for Al_2O_3 a 1:1 ratio was used. During the quarter, conditions were determined for routinely applying PyC coatings at a rate of $\sim 1 \mu m/min$ to minimize infiltration of the supercalcined waste structure and to preserve most of its inherent crushability. Propane at ~ 15 vol.% was initially used at 1200 to 1250°C to obtain the desired coating rate; however, this has recently been replaced by acetylene (~ 33 vol.%) at 1100°C to give the same coating rates for reasons discussed later in this report.

The PyC-coated waste particles were then overcoated with a porous Al_2O_3 coating (supplied at 550°C by the hydrolysis of $AlCl_3$) and then with a dense Al_2O_3 at 1050°C by the same chemical system. To improve the bond and nucleation characteristics of the Al_2O_3 coating, the PyC-coated waste particles were etched in steam at 550°C for 5 min in a fluidized bed before being overcoated. A graded-density Al_2O_3 coating was also applied to the PyC-coated material for evaluation by sequentially increasing the coating temperature from 550 to 1050°C.

Some of the techniques described above were determined to be a predictable solution to the cracking problem. It was found that even though infiltration was practically eliminated, the supercalcined waste particles were strengthened during the PyC-coating operation. Examination of waste particles heated in argon at temperatures (1200 to 1250°C) used in the PyC-coating operation revealed that the waste particles were grossly strengthened. It was this obvious requirement to apply the rapid-rate PyC coating at a lower temperature that prompted the switch to acetylene mentioned above. The application of a PyC coating at $\sim 1 \mu m/min$ from acetylene at 1100°C has resulted in Lot 32556-23-95, which appears to have a crack-free outer Al_2O_3 shell. This material has an 18 μm PyC layer, a 9- μm porous Al_2O_3 coating applied at 550°C, and an outer Al_2O_3 shell of $\sim 48 \mu m$ deposited at 1050°C. If this can suitably withstand an oxidation test, it will be shipped to BNW for further evaluation.

Previously used drum coating equipment has been located and preliminary design changes generated to make this equipment suitable for the needs of this project. This work has been deferred pending the preparation in a fluidized bed of duplex-coated specimens worthy of evaluation.

The lower temperature (500 to 600°C) Al_2O_3 coatings applied by the hydrolysis of AlCl_3 and pyrolysis of aluminum ethylate were both determined to contain connected porosity, which prevented their providing the required oxidation protection for the PyC-coated supercalcined waste. Conditions might be modified to provide a denser coating from the ethylate, but it is unlikely that a dense low-temperature coating can be obtained using the chloride precursor. Alumina coatings applied at 1100°C from the chloride were dense but did not offer any obvious advantage over those prepared at 1025 to 1050°C.

RADIATION DAMAGE (J. M. Rusin)

The purpose of this work is to determine the effects of radiation damage on the stability and physical properties of multibarrier waste forms.

Terbium and praseodymium-doped supercalcine has been studied in preparation for ^{244}Cm doping. Spinel, pollucite, and high ruthenium phases have been identified. Possible methods to transmute cesium to barium have been investigated.

In preparation for ^{244}Cm doping of supercalcine powder (SPC-2), cold samples doped with terbium and praseodymium have been pressed and sintered. Three batches were prepared: 1) SPC-2 with no additives, 2) SPC-2 with 3 wt% Tb_4O_7 , and 3) SPC-2 with 3 wt% $\text{PrO}_{1.83}$. The pellets were pressed at 7200 psi and were sintered at 1125°C for 2 hours.

The location of the terbium and praseodymium could not be determined by scanning electron microscope (SEM) x-ray emission. Large regions ($\sim 160\text{ }\mu\text{m}$) of spinel (iron, chromium, nickel) were identified as shown in Figure 9. At higher magnifications of 3000X, regions between 1 and 5 were identified as primarily pollucite ($\text{CsAlSi}_2\text{O}_6$), as also shown in Figure 8. Particles of a metallic nature, approximately 30 μm in diameter, were found to contain 100% ruthenium. These particles could either be metallic ruthenium or ruthenium

oxide. The terbium and praseodymium samples are presently being analyzed by XRD to determine if the additions caused any lattice parameter shifts.

SEM 3000X
Arrow indicates pollucite phase

Cs X-ray Map 3000X

Pollucite

SEM 3000X

Fe X-ray Map 3000X

Spinel

FIGURE 9. SEM and X-ray Mapping of Terbium-Doped SPC-2 Sample

In a short study conducted by U. P. Jenquin, neutronic calculations were performed to determine the transmutation rates of various isotopes of strontium and cesium to zirconium and barium, respectively. The neutron flux level used in the calculations corresponded to that in the HFIR at a radius of 26 cm. In this position the thermal flux is 1.5×10^5 n/cm²-sec and the epithermal flux from 0.5 eV to 0.1 MeV is 1.1×10^{15} n/cm²-sec.

With ⁹⁰Sr as the target for 96 days, only 1% of the atoms capture a neutron. Thus, the formation rate of zirconium is not increased appreciably compared to an unirradiated target.

Natural cesium exists as the isotope ¹³³Cs. It has a large resonance integral and a thermal cross section that is 30 times larger than the thermal cross section of ⁹⁰Sr. Thus, the capture rate by ¹³³Cs is large enough to feasibly form ¹³⁴Ba. If ¹³³Cs were irradiated for 100 days, 10.3% ¹³⁴Ba would be formed after 300 days subsequent decay time.

Other possible isotopes are ¹³⁵Cs, which, after a 48-day irradiation, converts 7.2% of the cesium to barium; and ¹³⁷Cs, which, if allowed to decay without being irradiated, would form 7.2% barium in 1200 days.

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

The purpose of this work is to determine the thermal, mechanical and physical properties of multibarrier waste forms for product optimization.

Thermal stability of supercalcine (SPC-2) is equivalent to or better than previous supercalcine batches. Loading of the cores in the metal matrix must be reduced to below 60% to provide a cushion of impact-resisting metal between the cores.

Vaporization

Supercalcine batch, SPC-2, has a drying loss at 110°C between 2.4 and 2.9 wt%. Thermal gravimetric analysis (TGA) shows a differential thermal gravimetric (DTG) peak at 50°C with a weight loss of 2.35% at 110°C. A very broad DTG peak is observed at 400°C to give a total weight loss of 9.02% at 900°C. The supercalcine powder vaporized at a constant rate of 0.049 wt%/hr for a period of 24 hours at 1100°C, resulting in a total weight loss of 1.18 wt%.

Supercalcine cores, SPC-2-A, previously sintered for 30 hours at 1100°C vaporized at a constant rate of 0.027 wt%/hr for a period of 24 hours at 1100°C, resulting in a total weight loss of 0.65%.

Vaporization rates will be studied at other temperatures. Vapor product will be collected on a cold finger for analysis.

Impact Resistance

Supercalcine in Sintered Stainless Steel

Five gravity-sintered 316 stainless steel matrix samples were impacted at 158.4 ft-lb. The samples used in the impact test were 0.52 in. in diameter by 0.50 in. long; they are identified in Table 6.

TABLE 6. Impact Test Sample Parameters

<u>Sample</u>	<u>Matrix, SST</u>	<u>Cores</u>	<u>Temperature, °C</u>	<u>Sintering Time, hr</u>
1	316	None	1050	20
2	316	0.049-in.-dia-sintered Al_2O_3	1050	40
3	316	0.049-in.-dia-sintered Al_2O_3	1050	40
4	316	0.046-in.-dia supercalcine 39- μm Al_2O_3 coating	1100	20
5	316	0.046-in.-dia supercalcine 67- μm Al_2O_3	1100	20

Quantitative results (e.g., screen analysis) are not available since it was difficult to separate fractured cores from stainless steel powder. In the future, a 410 stainless steel will be used that can be magnetically separated. General qualitative results are listed in Table 7.

In analyzing the results, it is important to note that maximum loading was used for the cores, i.e., the cores were in contact with one another. The sintered stainless steel matrix contains 50% porosity and the loading of the composite matrix was 60% cores, 20% stainless steel (-325 mesh) and 20% porosity.

TABLE 7. General Qualitative Results of Impact Tests
on Sintered Stainless Steel Composites

<u>Sample</u>	<u>Results of Impact</u>
1	Sample was rammed into the impact chamber being compressed to 0.120-in. thick.
2 & 3	Majority of cores were released from the matrix. Only a few were fractured.
4 & 5	Majority of cores were pulverized. Only a few cores remained intact and unfractured.

Since the cores were in contact, the metal matrix merely contained the cores and did not contribute to the impact resistance of the composite. Thus, the impact strength of the cores rather than the composite matrix was actually tested. As would be expected, the solid 0.049-in.-diameter-sintered alumina cores exhibit a much higher impact resistance than the 39- and 67- μm Al_2O_3 coated supercalcine. The initial impact cracks the Al_2O_3 coating since the cores are touching each other. As the impact continues the supercalcine cores are crushed because the continuous protective Al_2O_3 coating is no longer intact.

To test this theory another sample of matrix #4 was impacted at 158.4 ft-lb, but the ram could only travel 0.020 in. after contacting the sample. The sample remained intact after impact. Metallographs through the center of the sample illustrate not only cracks in the Al_2O_3 coating but cracks running through the supercalcine cores in the direction of the impact; see Figure 10. The metal matrix was unaffected by the impact. Thus, both the coating and the core are cracked by the initial impact and are destroyed before the metal matrix can contribute to the impact resistance.

Samples are presently being prepared with lower core loadings to provide metal matrix material between the cores. These samples will be impact tested.

8X

100X

FIGURE 10. Metallographs of Impacted 39-μm Al₂O₃ CVD-Coated Supercalcine in 316 SST Matrix

Glass in Metal Matrix

Matrix samples of 3 mm and 6 mm commercial glass balls and 10 mm 72-68 glass marbles in Pb-10% Sn have been impacted at 158.4 ft-lb. The samples were 1.25 in. in diameter by 1.25 in. high and were not contained during impact. The impact resulted in 20% compression of the samples accompanied by increased diameter and matrix stretching as illustrated in Figure 11. The glass balls and marbles are being removed from the matrix for particle-size analysis.

FIGURE 11. Impacted Marbles in Pb-10% Sn Matrix (mm-11-1, 3-mm commercial glass; mm 9-1, 10-mm-diameter 72-68 glass; mm 10-1, 6-mm commercial glass)

METAL MATRIX (K. R. Sump)

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

Aluminum - 12% silicon and lead were vacuum cast with 3- and 6-mm glass marbles. Pure metal samples were also made for characterization. The lead casting was done with the lead, mold, and marbles at 400°C. The aluminum - 12% silicon casting was done with the alloy at ~650°C and the mold and marbles at 550 to 600°C.

Good fill between particles was obtained in all vacuum cast samples. Previous casting studies using open quartz tubes did not fill as well, especially when the aluminum alloy was used as the matrix.

These preliminary casting results indicate that either lead, lead alloys or aluminum alloys can be used as the matrix for the low temperature glass marbles. Vacuum casting using Pb-10% Sn will be done in the near future.

The economics of aluminum versus lead in the cast matrix evaluation favors aluminum by ~2:1. The cost of Al-12% Si versus Pb-10% Sn favors the aluminum alloy by almost 5:1 because of the high cost of tin. Aluminum and its alloys are also stronger, have higher melting points and higher thermal conductivity values.

Several gravity-sintered 410 stainless steel samples were made at 1100°C for 8 hours in stagnant air. One of the samples had an ~60% loading of PyC/ Al_2O_3 clad supercalcine particles. Another had an ~40% loading of Al_2O_3 clad supercalcine particles. The samples will be used in impact tests.

SUPERCALCINE (G. J. McCarthy)^(a)

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

^(a) Pennsylvania State University, University Park, PA.

Characterization of Supercalcine 76-3 (SPC-2) (G. J. McCarthy, M. T. Davidson, D. E. Pfoertsch and R. G. Johnston)

Crystalline phase formation in SPC-2 fired in air was described previously.⁽²⁾ The phases identified by x-ray diffraction or other means were A_{ss} , F_{ss} , S_{ss} , T_{ss} , P , M_{ss} , $(Fe_2O_3)_{ss}$, SP_{ss} , and RuO_2 . We have observed full crystallization under processing conditions as minimal as 10 min at 1125°C or 2 hr at 1000°C. Consolidation of the SPC-2, as measured by pellet diameter shrinkage, was as effective with the latter treatment as with any of the 1000 to 1200°C, 2-16 hour firings. This evidence for good crystallization and consolidation with relatively brief and lower temperature heat treatment will be important input concerning the core crystallization/consolidation requirements for the process design of the multibarrier waste form.

A. A. Garrett of PNL finds that small additions of a montmorillonite-type clay (5 wt%) to SPC-2 improve the pelletizing process.^(a) In samples supplied by him, we find that the clay has little effect on the crystalline phase formation. The clay does appear to deplete somewhat the Sr concentration of S_{ss} , forming with it a small amount of an aluminosilicate phase tentatively identified as the anorthite structure polymorph of $SrAl_2Si_2O_8$. We are currently studying the effects of several levels of clay additions to SPC-2 on the leachability, cesium volatility and pressed-pellet consolidation.

Scanning electron microscope (SEM) characterization of cold-pressed (72,500 psi) and fired (1125°C, 2 1/2 hr) SPC-2 is in progress. To date, A_{ss} , P , SP_{ss} , and S_{ss} crystals have been identified in the specimens. Quantitative measurements of porosity on various specimens give values between 4 and 7 vol.%.

Soxhlet leachability has been measured on these cold-pressed and fired specimens. SPC-2 specimens as-received contained about 10 wt% of H_2O , NO_x , CO_2 . Several specimens were prepared from SPC-2 that had been prefired at 900°C for 2 hours to remove most of these volatile materials. The weight losses in a 72-hour test were 1.4% (2×10^{-5})^(b) for the as-received SPC-2

^(a) See page 25 of this report.

^(b) Leachability units in $g/cm^2/day$.

and 0.88% (1×10^{-5}) for the prefired SPC-2. These data indicate an approximately threefold decrease in leachability compared to the earlier supercalcine demonstration SPC-1.⁽⁵⁾

X-Ray Characterization of Coated Cores of 75-2 (SPC-1), (G. J. McCarthy and C. A. Smith)

Disc pelletized cores of the first engineering-scale batch of supercalcine, formulation number 75-2, were prepared by A. A. Garrett of PNL and forwarded to M. F. Browning of BCL for coating earlier this year. The following specimens of this type were studied by x-ray power diffraction in order to identify the crystalline phases present at this stage of the processing of the multibarrier waste form.

Supercalcine 75-2 (SPC-1) Coated with Pyrolytic Carbon (PyC)

Normal air-atmosphere crystallization of 75-2 yields products whose diffractograms show reflections of a very strong A_{SS} phase, a pollucite (P) phase with moderately intense reflections, and weak reflections of S_{SS} , F_{SS} , T_{SS} , and SP_{SS} . The diffractogram of the 75-2 pellets coated at BCL with PyC showed the usual sharp reflections of A_{SS} and P. Notably, the S_{SS} reflections were absent, indicating that either this phase was present below the level of detection by the x-ray method, or it had been modified during the production of the PyC coating. Several other moderate to weak reflections gave a good match to two carbide phases, Mo_2C and the solid solution phase $(Sr,Ba)C_2$. The reflections of these two phases, plus A_{SS} and P, accounted for all reflections in the diffractograms.

The PyC coatings are developed in a fluidized bed apparatus from a mixture of hydrocarbons and hydrogen. Possibly, the $(Sr,Ba)MoO_4[S_{SS}]$ phase was reduced to the metals, and these, in turn, reacted with the hydrocarbon to form the metal carbides. According to Hanson,⁽⁶⁾ Mo_2C and $(Sr,Ba)C_2$ are the most stable room temperature carbides of these metals. The tetragonal cell parameters of the dicarbide phase are far closer to those of SrC_2 than to BaC_2 , as would be required by the far greater concentration of Sr than Ba in 75-2. The next step in the characterization of these coatings would be to look for the Mo_2C and $(Sr,Ba)C_2$ phases by metallography or SEM/characteristic x-ray energy analyses.

Supercalcine 75-2 Coated with PyC and Al₂O₃

The phase assemblage identified from the ground pellets included A_{ss}, P, α-Al₂O₃, and reflections assigned to the proposed carbides, which were even stronger than observed in the previous PyC-only coated specimen.

Aluminum chloride was used as the source of aluminum in this run. The bed temperature was 1100°C. When aluminum ethylate is substituted for the chloride, a lower temperature can be used. A second sample of coated pellets prepared from the ethylate at 500°C was also studied. The phase assemblage was almost identical to that of the high temperature coated pellets, except that the α-Al₂O₃ reflections were less intense. It was a surprise to see several reflections that fit the α-Al₂O₃ pattern, because "α" is not the stable phase at this preparation temperature.

Supercalcine Formulations for High-Sodium Wastes (G. J. McCarthy and D. E. Pfoertsch)

Nepheline [Ne], NaAlSiO₄, has been selected as the sodium fixation phase. Two types of phase formation models are being developed for PW-7a-based supercalcines. The models differ chiefly by the crystal chemical role of the Rare Earths (RE). In the first model, the REs crystallize in an apatite structure solid solution [A_{ss}] phase and in the second, they crystallize in a monazite [M_{ss}] phase.

Compatibility of many of the phases of the nepheline-apatite model has been demonstrated:

<u>PW-7a Ion</u>	<u>Crystalline Phase</u>
Na, Mo, Sr	NaAlSiO ₄ and (Ca,Sr) ₂ [NaAlSiO ₄] ₆ (MoO ₄) ₂ [Ne] (So _{ss})
Cs(Rb)	CsAlSi ₂ O ₆ [P]
RE(La,Ce,Pr,Nd,Pm,Sm,Eu,Gd,Y) [PO ₄]	Ca ₂ RE ₈ [SiO ₄] ₆ O ₂ and REPO ₄ [A _{ss}] [M _{ss}]
Zr, Fe	(Zr,...)O ₂ Fe ₂ O ₃ [T _{ss}]

Little or no alkali volatilization was observed during crystallization of these phase assemblages at 950 and 1050°C. Other compatibility studies involving cesium, uranium, barium, and chromium are in progress.

In a second phase formation model also being evaluated, the REs are crystallized completely in $\text{REPO}_4[\text{M}_{\text{ss}}]$. Here, phosphoric acid replaces some of the silica as a supercalcine additive.

Progress was made on understanding the crystal chemistry of the sodalite structure solid solutions $[\text{So}_{\text{ss}}]$, the monazite structure solid solution $[\text{M}_{\text{ss}}]$ and high-sodium $[\text{A}_{\text{ss}}]$ phases.

Tellurium in Supercalcine

A literature survey yielded information on several potential phases for tellurium crystallization in supercalcine. Attempts were made to synthesize these as pure phases. Many of the promising compounds or solid solution phases either did not form under typical supercalcine crystallization conditions, or they lost tellurium during firing. The compound Ca_3TeO_6 is a very stable, refractory tellurium phase. Unfortunately, it appears that Ca_3TeO_6 is not compatible with pollucite. We will soon be looking into partial (TeO_4) substitution for (MoO_4) in So_{ss} .

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