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**Quarterly Progress Report
Research and Development
Activities Waste Fixation
Program
January Through March 1976**

by
J. L. McElroy

**Prepared for the Energy Research
and Development Administration
under Contract E(45-1)-1830**

Battelle
Pacific Northwest Laboratories

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QUARTERLY PROGRESS REPORT
RESEARCH AND DEVELOPMENT ACTIVITIES
WASTE FIXATION PROGRAM
JANUARY THROUGH MARCH 1976

By
J. L. McElroy
Chemical Technology Department

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QUARTERLY PROGRESS REPORT
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WASTE FIXATION PROGRAM
JANUARY THROUGH MARCH 1976

INTRODUCTION

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

SUMMARY

Two engineering-scale in-can melting tests were made which demonstrated melting capacities of 30 kg/hr in an 8-in. diam canister and 50 kg/hr in a 12-in. diam canister. These rates are just in excess of those necessary to meet the needs of the NFS plant reprocessing 2.5 MTU/day and the AGNS plant reprocessing 5 MTU/day.

The Developmental Spray Calciner was operated for 19 hr to calcine simulated AGNS ILLW waste, evaluate the blowback system, and support an in-can melting run.

Several short runs with the fluidized bed calciner were completed to demonstrate the operability of the continuous inert bed process. All equipment operated extremely well including the new tube feed nozzle and sintered metal off-gas filters. Product characterization work was completed, giving some insight into the process behavior.

The engineering scale ceramic melter was modified, restarted and since restart has been at operating temperature for 62 continuous days. Several calcine feeding tests were completed and 1,000 lb of glass were produced. While melting a high resistivity glass, shorting through the refractory was encountered.

A canister weighing system was installed to monitor the accumulation of glass products in the receiving canister of the development in-can melting system. While the weighing system was designed to monitor canisters weighing up to 500 kg, incremental weight changes of 0.5 kg were readily detected, and total weight changes of 200 kg, measured during operation, were accurate to within one kg.

A composition has been selected for PW-8a waste for further characterization. During devitrification no microcracking has been observed. The use of silicon metal powders as a reducing agent in the glass produces significant reaction heat, but does not constitute a heat generation hazard.

Concentrations of major crystalline phases in glass 72-68 (1000°C melt) have been established as a function of annealing time ($t < 2$ months) and temperature (300-900°C). The Zn_2SiO_4 and $(\text{Ca}, \text{Sr}, \text{Ba})\text{MoO}_4$ devitrification products reach maximum concentrations of 14 and 6 wt%, respectively, at temperatures in the 600-800°C range, depending on the annealing time, while RuO_2 and $(\text{Ce}, \text{Zr})\text{O}_2$ remain at constant concentrations of 2 and 5 wt%, respectively.

Tests showed that measurement of electrical resistance at temperature over long times appears to be a potentially valuable method for investigating the devitrification of nuclear waste glasses.

The density of PW-7a waste glass was measured from 500 to 1100°C and an equation was developed expressing the dependence of density on temperature.

Waste from processed enriched UO_2 fuel pellets irradiated to an average burnup of 54,000 MWd/MTU has been vitrified in an in-can melter and wafers sectioned from the filled can were found to be of good physical quality.

Three HLW glass runs were made and stratification of isotopes appears consistent in all three, with the top being of significantly higher radiation than anywhere else.

Studies showed that increase in porosity of 72-68 glass at higher storage temperatures is a result of microcracking caused by Zn_2SiO_4 crystals in the glass matrix.

Elemental silicon or Zircaloy additions to melt increase the corrosiveness of the system to 304L stainless steel. Intergranular attack is initiated; however, the depth of penetration in 48 hours at 1050°C is only 2 to 3 mils. Chloride addition to melt at 1050°C at the 1% level has no effect on the corrosiveness of the system, whereas fluoride at the same concentration increases corrosion of 304L by a factor of about eight.

Current waste particle coating efforts are directed toward the development of high quality Al_2O_3 coatings on larger (1 to 10 mm) pellets. The latter, some of which are made from Pennsylvania State's supercalcine, are produced in a disc pelletizer.

The disc pelletizer successfully produced pellets of supercalcine, some of which were subsequently sintered. Pellets fired at 1200°C were rugged and yielded densities around 3.7. The supercalcine gives a waste loading of about 50 wt% in the pellets.

At Pennsylvania State University, studies were made to learn more about the rare earth silicate-phosphate apatite structure phase which is the dominant species in crystallized supercalcine and on consolidation methods for the PW-4b-based spray supercalcine prepared at PNL. The first steps have been taken toward development of supercalcine formulations for PW-7-based wastes.

A report describing the risk-based fault tree analysis method for the identification and preliminary evaluation of potential radionuclide release sequences was published. Initial application of the method revealed that dominant sequences of the Year 2000 high-level waste management system that could conceivably have significant public health and safety impact are highly improbable, one accidental release per million years or less.

SECTION 1.0 COMMERCIAL WASTE FIXATION

The purpose of this task is to develop processes and equipment for converting liquid-high-level radioactive waste to a stable, relatively non-dispersible form for storage and, ultimately, disposal. This objective is generally being accomplished by development of a two-step approach, calcination 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, vitrification of a mixture of calcined nuclear waste and glass-forming frit using the storage canister as the melting crucible.

The main objective of the two in-can melting runs made during the last reporting period was to establish the maximum melting capacity of the in-can melting process for 8- and 12-in diam cans incorporating the reference fin design as shown in Figure 1.1. The cans were made of 304L stainless steel.

The empty cans were suspended in the furnace from a load cell with the upper 18 in. of each can extending out of the heated chamber through a 6-in. thick insulating collar. The cans were coupled to the spray calciner with the coupling section described in the last quarterly report.⁽¹⁾ A metal bellows in this section allows the can to hang free from the load cell. A valve in the coupling section, resembling an inverted funnel, compresses the bellows when closed; thus disconnecting the coupling section from the can and at the same time sealing off the coupling. When opened, the valve acts as a baffle in the neck of the can and disperses incoming batch away from the center of the can to the hotter perimeter.

The empty cans were heated to between 1045 and 1135°C and then fed a preblended batch of one part simulated AGNS HLW ILLW type waste calcine (PW-7a)⁽²⁾ and two parts borosilicate frit (75-75) with 1.5 wt% powdered silicon metal added. An average melting rate of 26.3 kg/hr was demonstrated for 1-2/3 hr with the peak rate of 27.5 kg/hr being maintained for 1/2 hr in the 8-in. diam

FIGURE 1.1. Typical In-Can Melter Test Canister

can. These rates represent the maximum output rate of the batch screw feeder and not the capacity of the melter. The melter maximum power consumption at this time was only 17 kW, and the center-line temperatures measured by thermocouples dropped only 20 to 60°C as the melt level rose over them; indicating that the melting capacity of the 8-in. diam finned can was not being exceeded. It is safe to say that the 8-in. in-can melter is capable of melting at the rate of at least 30 kg/hr under the conditions of this demonstration.

An average melting rate of 42.7 kg/hr was demonstrated for 3-1/4 hr with a peak rate of 50 kg/hr being maintained for 1/2 hr in the 12-in. diam can. The thermocouple located in the center of the canister at the melt level when the batch was entering at the 50 kg/hr rate showed a temperature decrease from

1000°C to 930°C before starting to rise again. Thus, 50 kg/hr is believed to be the maximum capacity of the 12-in. diam, finned in-can melter under the conditions of this demonstration.

The conditions which contributed to these melting capacities for the in-can melter are:

1. The canister surface temperatures of 1045 to 1130°C. The effects on the 304L stainless steel of operating in this temperature range are still being evaluated, but no gross canister distortion has been observed.
2. The eight internal, radial fins. Figure 1.2 shows the difference that the internal fin assembly makes in the melting capacity of the in-can melter. They more than double the melting rate even though they are actually designed for heat dissipation during storage and transport of the canister of glass.
3. The use of the rising level melting process, which is simply continuously charging the melter with batch at a rate equal to or just less than the melting rate, instead of the batch melting process. Experience has shown the rising level melting process is capable of melting rates that are double those achieved by a batch melting process.
4. The 1.5 wt% powdered silicon metal in the batch which releases heat as it oxidizes and prevents the formation of soluble alkali metal molybdates. The energy required to melt the batch without silicon was between 225 and 306 cal/g while only 120 to 200 cal/g were required to melt the batch containing silicon at a rate double that formerly achieved.
5. The coupling section valve which deflects feed toward the hot walls of the can. During the first few hours of the demonstration the valve was located 17 in. above the top of the fins so that it did not obstruct the view port. Bridges of batch rapidly formed across the top of the fins near the center of the can and batch charging had to be interrupted every 1/4 hr to allow them to melt away; however, when the valve was lowered to a position 11-1/2 in. above the fins, no bridges formed and batch charging rates as high as 50 kg/hr were sustained for over three hours. The valve not only acts as a batch disperser, but it also is an insulating plug which reduces heat losses out the top of the can.

FIGURE 1.2. In-Can Melting Capacities

6. A resistance band heater was placed around the outside of the can at the top of the fins. This heater compensates for heat lost out the top of the furnace and simulates the operating method that will be used with the multizone furnace scheduled for delivery later in 1976.

In addition to the melting capacity data gathered from these in-can melts, other studies were also conducted. One canister was air quenched from 745°C and another was water quenched from 760°C. The effects of these quenches on the can materials and the vitrified product are still being evaluated.

Spraying the inside surfaces of the can above the melt level with water while the full can was still at the glass melting temperature was tested as a

method for removing the calcine-rich material that collects there during charging of the melter. This material has a high leach rate compared to the vitrified product and accumulates as spall on the surface of the product as the can cools.⁽³⁾ Although the spray did cause some spall to fall from the sides into the melt, it also generated large quantities of steam and solids in the off-gas.

During the filling of part of one can, the frit was intentionally shut off for specified periods to allow the accumulation of layers of calcine 1, 2, and 4 cm deep between 10 cm layers of the melt. This was done to determine how long the frit-to-calcine ratio could be out of control before an unacceptable product developed. This information will be used to determine the precision required for the process control equipment such as the load cells used to monitor the rate of weight change of the in-can melter contents. When the can of vitrified product was opened for inspection, no strata were present. However, inclusions as large as 2 cm, which are believed to be calcine rich, were dispersed throughout the product and at the bottom of the can. Analyses are being performed to determine their composition.

DEVELOPMENTAL SPRAY CALCINER - L. S. Romero

The objective of this work is to provide commercial nuclear fuel reprocessors a reliable system for drying radioactive liquid waste prior to vitrification.

One calciner run was made to evaluate the calcination of simulated AGNS ILLW. The feed composition is shown in Table 1.1. A total of approximately 65 ℓ at the rate of 15 ℓ /hr was calcined with a few minor problems. The problems encountered were not related to the spray calciner unit; however, a ceramic nozzle was seen to be fractured when inspected after the run. The ceramic nozzle had accumulated ~900 hr on the test station and 50 hr on the spray calciner with no signs of wear (<0.5 mils). The nozzle fractured due to lack of atomizing air which normally cools the unit and prevents thermal shock. Air flow was restored by simply opening the closed valve on the atomizing line. (The valve had been closed for operation of other equipment not related to the spray calciner.)

The product varied from the usual fine powder to flat crusty chunks approximately 1/16 in. in diameter. The chunks easily disintegrated to powder when touched. The calcine produced contained about 31 wt% sodium and 9.7 wt% nitrate.

TABLE 1.1. Simulated AGNS ILLW Feed Composition

AGNS ILLW as defined Element	at 283 ℓ /MTU M	Substitute Element	M	Chemical
Pu	0.0001	rare earth*	0.0301	rare earth nitrate
U	0.0300			
Na	0.76	---	0.76	NaNO_3
Fe	0.0025	---	0.0025	$\text{Fe}(\text{NO}_3)_2 \cdot 9\text{H}_2\text{O}$
Ag	0.0003	**		
PO_4	0.24	---	0.24	H_3PO_4 (100%)
Mn	0.0088	Mo*	0.0088	MoO_3
K	0.0054	---	0.0054	KNO_3
SO_4	0.0063	**		
Cl	0.016	**		
F	0.0013	**		
Hg	0.0229	**		
I	0.0069	**		

* Stand-in elements substituted on a mole for mole basis.

** Not used or substituted.

The filters were coated with a layer of calcine that did not blow off during the run and gradually increased the pressure drop. On visual inspection the calcine layer showed signs of moisture possibly caused by blinding the filters when the feed was not atomized at the start of the run. However, later tests showed that this waste can be calcined without adversely affecting filter operation.

Other than the minor problems encountered, the spray calciner successfully simulated AGNS ILLW waste. Visual inspection of the spray chamber showed no signs of fouling.

The objective of another test run was to evaluate the filter blowback system by relocating the solenoid valves approximately 15 ft from the venturi nozzles. The blowback system was evaluated under normal and an altered condition for approximately 10 hr at a calciner feed rate of 18 ℓ /hr. Under normal conditions, the blowback was set at a 2-min cycle with a 1/4-sec pulse and 60 psig blowback air while in the altered condition, the blowback cycle was increased to an hour with a 1/4-sec pulse of 80 psig air.

When the filters were blown back every 2 min, the pressure drop across them gradually increased from 12 to 14 in. of H_2O by the end of the run. When blown every hour, the pressure drop increased from 12 in. of H_2O to approximately 16 in. of H_2O within an hour; however, the filter returned to a "clean filter" value of 12 in. of H_2O after each blowback.

The above data indicate that the filters can be effectively cleaned with a blowback cycle of over an hour and with solenoid valves located as far as 15 ft away from the venturies.

FLUIDIZED BED CALCINATION - W. J. Bjorklund and F. E. Haun

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

PW-7a and PW-8a waste types, representing proposed AGNS and NFS HLW compositions were calcined using the inert bed process. Operating data for the runs are shown on Table 1.2. Product characterization work was aimed at determining the fate of the sodium in the waste: whether it is an oxide, nitrate, ferrate or silicate. It appears, as suspected, that the sodium is reacting with the silicate but the reaction is not complete. Product from run 17 (1.0M Na, 0.65M Fe) was analyzed to see if sodium ferrate was forming, but an insignificant amount was found.

TABLE 1.2. Operating Conditions for Fluidized Bed Calciner Runs, January - March, 1976

<u>Run Number</u>	<u>15</u>	<u>16</u>	<u>17</u>	<u>18</u>
Feed On (hrs)	6.7	6.2	6.5	4
Feed Rate (ℓ/hr)	20	21.6	20-25	20-35, 26 Avg
Feed Type	PW-7a-2 150 g oxide/ℓ 0.5 <u>M</u> Na	PW-7a-2 174 g oxide/ℓ 0.64 <u>M</u> Na 0.13 <u>M</u> Fe	PW-8a 207 g oxide/ℓ 1.0 <u>M</u> Na 0.64 <u>M</u> Fe	PW-7a-2 178 g oxide/ℓ 0.6 <u>M</u> Na
Feed Nozzle Air-Liquid Atomizing Ratio	500	200-520	320-400	240-425
Bed Temperature (°C)	500-545	550	575	540
Fluidized Velocity (ft/sec)	0.98	0.98	1.08	0.96
Filter ΔP (in. H ₂ O)	6-8	7-15	8-12	10-15
Permeability (ft/min - in. H ₂ O)	0.4-0.5	0.2-0.4	0.26-0.37	0.25-0.43
Feed Nozzle	Tube Type	Tube Type	Tube Type	Tube Type
Fuel Nozzle	Spraying Systems Internal Mix	→	→	→

Photo micrographs were taken of the inert bed material and calcine during various phases of the CIB operation. These photos are shown in Figure 1.3. The silica (SiO₂) starting bed and inert addition material is initially round and regular. It is cracked during operation most likely from thermal shock (or possibly phase change) as it is rapidly heated to the bed operating temperature. The operating bed is coated with calcine to various degrees but typically the bed is 70-80% inerts. The product consists of overflowed bed material and elutriated fines. The fines are obviously richer in calcine.

JOULE HEATED CERAMIC MELTER - C. C. Chapman

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

After the melter had been examined, following shutdown due to a building power interruption, a few design modifications were made which were intended to improve the operability of the unit. The modifications made can be better

Starting Bed and Inert Addition
Material - SiO_2 (50X)

Bed Plus Overhead (50X)

FIGURE 1.3. Bed Material During Operation (50X)

understood by examining Figure 1.4. At the top of the figure, is a plan view of the melter before the modifications. The numbered descriptions which follow correspond to the encircled identification numbers in Figure 1.4.

1. One overflow electrode was removed along with a portion of the sidewall (cross hatched area). A refractory block with a 3-in. high by 6-in. wide cutout was placed in the sidewall (see view A-A).
2. The overflow electrode removed in the above step was placed on the opposite sidewall. In this arrangement, the current flows across the melting cavity through the cutout in the opposite sidewall around the stand pipe to the other electrode.
3. A sleeve 3-in. outside diam was slipped over the old 2-in. diam drain pipe. This in effect repaired the damage, which occurred to the 0.125-in. thick lip on the old stand pipe. The 1/2-in. wall thickness should provide extended service.

FIGURE 1.4. Schematic of Melter Modifications

After these modifications, 5 parallel coils of resistance wire were placed between the faces of the main electrodes. These coils were buried in frit and used to start up the melter which was accomplished in less than 4 hr without problems. Since startup, the melter has processed over 980 lb of glass. In one experiment a glass with low sodium content was melted and after about 4 hr of melting, shorting through one sidewall was noted. Recovery from the shorting condition was achieved by adding sodium hydroxide to the pool. From this experiment it was verified that the present high chrome oxide refractory is not suitable for melting glasses with high electrical resistivity. Based on this information, future melters will be constructed from materials that have much higher electrical resistivity.

ICM INSTRUMENT SUPPORT - R. D. Dierks

The information being obtained in this study is intended to aid in developing design specifications for instrument monitoring systems for equipment to reduce nuclear fuel reprocessing high-level liquid wastes to a borosilicate glass product, suitable for long-term storage.

A canister weighing system was installed in the development in-can melter facility to evaluate the possibility of using the canister weight to detect compromising process conditions such as canister overfilling, frit feeder failure, calcine/frit holdup within the calciner, or inappropriate calciner-to-frit addition ratios. The canister support system was modified to suspend the canister free of the furnace from a single, 0-500 kg, strain gage-type load cell, attached to a solid overhead structural member. A metallic bellows in the canister fill head assembly minimized the effect of the connection between the canister and the calciner on the response of the weighing system. A vacuum compensator system supplied an additive signal, proportional to the calciner vacuum, to the output of the load cell indicator to compensate for the portion of the canister weight that is supported by the calciner vacuum (about 0.5 kg/in. of water vacuum).

Due to the high speed of the calciner vacuum fluctuations, and the non-matching response speed of the vacuum compensation system, a continuous fluctuation of the indicated canister weight limited the interpretation of the indicated weight to ± 0.25 kg. Improvement of the compensation system should minimize the fluctuation of the indicated canister weight and improve the resolution of the weighing system.

During the in-can melting experiment ICM-16, 180 kg of glass was indicated as having been added to the canister by the weighing system, as opposed to a weight increase of 179 kg as calculated from platform scale values logged before and after the experiment. The glass-filled canister totaled 340 kg.

In the early development of the in-can melting system, particularly when using the slurry feed from the wiped film evaporator, bridging was observed across the tops of the canister fins, with the ultimate formation of a difficult-to-melt cold cap sitting on the fins with a void below the cap. With modified canister and furnace designs, and with feed materials limited to dry calcines, bridging is no longer observed. However, a small radiant heat sensor has been positioned in the canister fill head assembly to sense the formation of a cold cap in the event of off-standard melter system operations. The sensor consisted of two, 3/4-inch diam stainless steel discs, positioned one behind the other and looking down into the canister. Insulation separated the two discs, and both were recessed into an insulated cavity to limit side view. Thermocouples measured the temperatures of the discs and their difference was, in part, representative of the radiant heat seen by the lower disc. The sensor was operated during two ICM experiments and while the output from the sensor was quite active, no correlation of the output to the operation of melting system was readily apparent. Additional tests are planned with a modified sensor.

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SECTION 2.0 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 HLWs in durable glasses at low processing temperatures.

The development of low ZnO-containing melts continued with tests on the effect of various alkalis, PbO, TiO₂, and Si metal. A composition was selected and has been given initial characterization tests.

Glass Composition

The major emphasis of glass development has been with the PW-8a composition reported during the last period. The PW-8a behaves similarly to PW-8 in glass except the lower Fe₂O₃ has allowed lower leach rates to be obtained and less alkali is required in the frit. The basic glass batch composition for PW-8a with which additional tests are being made is composed of:

38.5%	SiO ₂
1.5%	Si
9.5%	B ₂ O ₃
2.0%	CaO
5.0%	ZnO
3.0%	TiO ₂
7.5%	Na ₂ O
33.0%	PW-8a-1

It was determined that Li_2O additions tend to promote phase separation in the glass and have therefore been eliminated in the 76-76 composition shown above. The addition of TiO_2 , a nucleating agent commonly used to form glass-ceramics, resulted from its beneficial effect on both viscosity and durability. Its effects on devitrification are currently being tested.

Lead oxide additions produce low melting glasses and previous tests have shown PbO glasses to have good durability as measured by the soxhlet method. More recent tests have shown that high concentration of PbO can lead to a glass with low resistance to acid attack. One further problem with PbO melts is that PbO is more easily reduced than MoO_3 which eliminates the potential of using reducing additives such as silicon to control Na_2MoO_4 formation.

Silicon Additions to Melts

Tests on the effects of silicon additions on glass melts have been made to determine process limits. Since the silicon produces a strong exothermic reaction significant heat can be generated. Tests were performed with addition of up to 4.5 wt% -325 mesh silicon powder to note the maximum amount of silicon which could be used without exceeding the normal 1050°C melting temperature of the glass. The tests showed that even the 4.5 wt% addition was not sufficient to heat the total glass batch to 1000°C and that increases in the amount of silicon used would significantly reduce the time required to melt a glass batch. This is shown in Table 2.1 where time is that required for the center of a 6-in. diam canister to be heated from 130°C to 1000°C in a furnace at 1050°C .

TABLE 2.1 Effect of Silicon Content on Melting Time

<u>Silicon Content</u>	<u>Melting Time</u>
0 wt%	105 min
1.5 wt%	80 min
3.0 wt%	20 min
4.5 wt%	7 min

It was again observed that with both the 3 and 4.5 wt% additions of silicon that zinc was reduced and volatilized. Some melt development work is being directed to forming non-zinc glasses to prevent zinc volatility and its potential corrosion problems.

A second series of tests with various size fractions of silicon metal powders showed that larger particle sizes do not completely react during the normal melting time of two hours and can produce additional stresses in the glass. Future work will continue to use -325 mesh powders to avoid these problems.

Characterization Data

Leach rates in acid and basic solutions for the current glasses are 3×10^{-6} and 6×10^{-6} gm/cm²-day respectively. The effects of devitrification and phase separation on both PW-8 and PW-8a glasses are being determined by holding them in a stainless steel tube in a thermal gradient from 400°C to 1000°C for one week. Sections which were exposed to desired temperatures are then subjected to leach tests and metallography. The leach results have not shown any temperature range to increase the leach rate an order of magnitude as measured by standard acid, basic, or neutral water tests. More detailed tests with isothermal sections will be conducted later.

Metallographic examination of these glasses has shown that some of the undissolved crystalline material can settle in the glass at temperatures in excess of 800°C. Figures 2.1 and 2.2 show sections of the PW-8 glass held at 750 and 800°C. These micrographs show that some crystals are forming in the glass, but they are not large enough to produce any microcracking in the glass as was observed with the high ZnO glasses where Zn_2SiO_4 was formed. A more detailed examination is being made to identify the crystal species that are forming.

The viscosity of the basic glass composition was tested and found to be 150 to 200 poise at 1050°C. The variation is due to difference in shear rate used for the measurements and demonstrates that the undissolved material in the glass makes the viscosity non-Newtonian.

FIGURE 2.1. 200X Micrograph of PW-8 Glass Held at 750°C for One Week

FIGURE 2.2. 200X Micrograph of PW-8 Glass Held at 800°C for One Week

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

This task is directed toward general understanding of the glass making and devitrification processes, primarily through microstructural examination (including microprobe analysis) and x-ray diffraction methods.

This quarter, we have completed quantitative analyses of samples from the long term thermal effects study of glass 72-68 (1000°C melt). Good agreement was obtained between the microprobe and x-ray diffraction methods except at lower temperatures for reasons discussed later. The $(\text{Ce,Zr})\text{O}_2$ and RuO_2 phases do not change with time or annealing temperature from their concentrations in the original melt of 5 and 2 wt%, respectively. The Zn_2SiO_4 and $(\text{Ca,Sr,Ba})\text{MoO}_4$ devitrification products reach maximum concentrations of 14 and 6 wt%, respectively.

Devitrified glass samples annealed for times through two months were examined on the microprobe, analyzing the glass matrix for depletion of Zn, Sr, and Mo and by x-ray diffraction for concentrations of the crystalline phases. The microprobe work was done on polished samples at 500X-2000X, taking care to avoid regions where any second phase crystals could be seen. From 3 to 5 analyses were made on each sample with a statistical error of $\pm 2\%$ for Zn and $\pm 4\%$ for Sr and Mo. In the x-ray method, calibration curves were obtained for Zn_2SiO_4 , SrMoO_4 , and CeO_2 , establishing reproducibility to ± 0.5 wt% and a detection limit of ± 0.3 wt%.

Figure 2.3 shows probe results for Zn, as a function of time at the various annealing temperatures. It is clear that little reaction occurs at or below 500°C and that equilibrium is rapidly achieved at 700°C and above. Figure 2.4 compares the x-ray and probe results after the two month anneals, with excellent agreement in the 700-900°C region. At 600°C, the crystals are too small and evenly distributed for the microprobe to avoid, so that an erroneous, low matrix depletion value was obtained. Figure 2.5 shows the x-ray diffraction results for SrMoO_4 which again are different from the probe results (not shown) primarily at 600°C where the probe values are too low.

FIGURE 2.3. Microprobe Results for Zn Depletion in the Glass Matrix Plotted as Relative Concentration Versus Time for the Temperatures Indicated ($^{\circ}\text{C}$).

FIGURE 2.4. Comparison of Microprobe and X-ray Diffraction Analyses for Formation of Zn_2SiO_4 as a Function of Temperature, After Two Months Annealing.

FIGURE 2.5. X-ray Diffraction Results for $(\text{Ca}, \text{Sr}, \text{Ba})\text{MoO}_4$ Formation as a Function of Temperature After Two Months Annealing.

Some other features of the devitrification process have been clarified:

- Settling of crystalline phases does occur at 900°C after two months storage. Concentrations for the top and bottom sections (~ 2 inch tall samples) are as follows (wt% top/wt% bottom): Zn_2SiO_4 (4.5/5.3), CeO_2 (3.5/5.7), and RuO_2 (1.3/2.1).
- The molybdate phase changes in composition with time. After one day at 750°C, the composition was $(\text{Ca}_{0.32}\text{Sr}_{0.56}\text{Ba}_{0.12})\text{MoO}_4$ and after two months at 750°C it was $(\text{Ca}_{0.23}\text{Sr}_{0.56}\text{Ba}_{0.21})\text{MoO}_4$.
- In samples annealed two months at 300-500°C, a rod shaped phase (~ 2 μm long by 0.2 μm diam) easily removed from polished samples by water rinsing, is a molybdate, probably containing Ca, Sr, Ba, as above. Although below the detection limit by x-ray diffraction (i.e., <0.3 wt%), this phase probably accounts for increased leachability observed for these anneal times and temperatures.

- In samples annealed two months at 700-800°C, a new hexagonal phase is present in significant concentrations. Microprobe analysis gave the following compositions, in wt%: Nd (22.1), Pr (9.8), La (9.6), Sm (3.6), Gd (2.3), Si (8.3) giving a molar basis (rare earths)/silicon ~1. There are no significant concentrations of Ca, Sr, or Ba, nor the alkali metals, ruling out an apatite related phase, often seen by McCarthy (Penn State) in SiO₂ containing-calcine formulations.

During the next quarter we will complete the short time kinetic study of glass 72-68 (1000°C melt, 1200°C melt) as compared to the calcine free glass frit, for ingrowth of the Zn₂SiO₄ phase. In addition, examination of the phase behavior in the next generation glass composition will begin.

Phase Behavior: Devitrification and Electrical Resistivity - J. L. Bates

Devitrification of nuclear waste glasses can occur at the high storage temperatures and at long times. Knowledge of the magnitude and rate of devitrification is important to understanding the properties of the waste product as it pertains to the long-term stability. Previous experience has shown that electrical resistivity changes during cooling as the crystalline phases appear in the simulated nuclear waste glasses. Therefore, by measuring the electrical resistance at temperature as a function of time, and correlating the results with the microstructural and x-ray diffraction studies of the devitrified glasses it appears possible to determine directly devitrification rates and processes.

The glass is melted in a small platinum crucible and two platinum wire electrodes are inserted into the molten glass. The glass is then rapidly cooled to the desired temperature to ensure a totally vitreous glass at the start of the test. The electrical resistance of the glass between the two electrodes is measured with an ac current at 40 and 1000 Hz at constant temperature. All measurements are made in air.

The results for the 73-1 glass frit* (without waste) is presently being studied to generate a reference base for comparing glasses containing simulated

* The 73-1 glass frit contains 37% SiO₂, 28.9% ZnO, 15.1% B₂O₃, 5.5% Na₂O, 5.5% K₂O, and 2% each of CaO, MgO, SrO, and BaO.

waste. Some initial results at three temperatures are shown in Figure 2.6. Although preliminary, the resistances, as expected, approach constant values with time, with longer times required at the lower temperatures to reach constant values. Unexpected, but consistent at the three temperatures, are increases in resistance during the first few hours of the annealing period, followed by irregularities in the resistance-time curve. At longer times, the decrease in resistance with time is smooth.

FIGURE 2.6. Electrical Resistance of 73-1 Glass Frit at 1000 Hz (not all data points shown)

The measurement of electrical resistance at temperature appears to be a potentially valuable method for investigating the devitrification of nuclear waste glasses. Further measurements and evaluation are continuing.

Physical Properties of Waste Glass: Liquid Density - J. J. Rasmussen

The density of solid and molten simulated waste glass was determined from near room temperature to 1100°C. The density was measured using a

radiographic volumetric technique.⁽¹⁾ Right cylinders, 0.97 cm diam and 5.1 cm long, were cut from solidified waste glass* melted and solidified in a waste canister. These cylinders were inserted in 1.02 cm internal diam, 7.62 cm long graphite crucibles. The sample and crucible were placed in a tungsten resistance heated furnace for examination radiographically as a function of temperature.

The furnace was allowed to reach a constant temperature and equilibrate thermally, and a radiograph was exposed. The temperature was then increased and again radiographed. The density was calculated from the height and diameter of the waste sample corrected for thermal expansion. Below 500°C, the diameter was corrected using thermal expansion data obtained by using a push rod dilatometer. Above 500°C, the diameter of the waste sample was determined from the I.D. of the graphite crucible corrected for the thermal expansion of graphite. The waste did not wet the graphite crucible initially and formed a convex meniscus. After a period of heating and cooling, the meniscus began to change shape and eventually formed a concave meniscus indicating the waste was wetting the graphite. The volume of the waste in the meniscus was calculated from the relation for the volume of an ellipsoid, $V = 4/3 \pi abc$ where a, b, and c are the semiaxes of the ellipsoid. Two of the axes represent the radius of the crucible and the third axis is the height of the meniscus.

Measurements were made in one atmosphere of argon. An attempt to obtain data by heating under vacuum was also made, however, no data could be obtained due to outgassing from the sample. So many bubbles were released starting at 500°C that the sample-vacuum interface was completely lost on the radiographs.

The density results for two waste glass samples are shown in Figure 2.7. At temperatures above 500°C the data points obtained during the initial heating of samples WG1 and WG3 were indistinguishable. After heating above 600°C, the measured density versus temperature curve can be extrapolated back to the original room temperature density points. The density measured at 500°C on

* ICM-12 canister with PW-7a-2 (1:2) 75-75+1.5% Si.

cooling sample WG3 was observed to fall on the density versus temperature curve. However, the data points measured on the initial heating below 500°C for both WG1 and WG3 fell well above this curve. These nonlinear density values can occur if the glass is either in the viscous flow range and is beginning to slump under its own weight or if the original glass from which the sample has been cut has been cooled rapidly and was contracting under imposed stresses induced on cooling. This contraction would cause an apparently high density before equilibrium was reached. A clear exposure of the sample radius in the temperature range around 500°C would help to clarify the density behavior. However, interference from the radiation shields prevented this.

FIGURE 2.7. Density of Waste Product PW-7a-2 (1:2)
75-75+1.5% Si from Waste Canister ICM12

The density points on the second heating of WG3 followed the previously established curve. However, at 1000°C bubbles began to form at the bottom of the sample and rise through the glass. The density began to increase as the

volume decreased with the gas loss. Upon cooling the density measurements followed a curve which is essentially parallel to the heating curve but displaced upwards to a higher density region.

The density results measured above 500°C show that the actual waste densities are much lower than those calculated by extrapolating thermal expansion data beyond the glass transformation range. Gases also appear to be trapped in the glass or are formed if the glass reacts with the graphite forming CO₂. These gases are released at 950-1000°C under one atmosphere of argon and at 500-600°C in vacuum. The temperature (T, °C) dependence of the density (ρ , g/cm³) can be expressed:

$$\rho = 3.32 - 3.4 \times 10^{-4}T \quad (1)$$

FULL-LEVEL RADIOACTIVE TESTS

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

Full-Level Radioactive Glass Specimens: Waste Preparation - E. J. Wheelwright and R. D. Scheele

Preparation of the solid waste has now been completed, and these solids delivered to Y. B. Katayama in the 324 Building.

Briefly recapping the program, 2764 g of LWR UO₂ fuel were dissolved in nitric acid. The undissolved solids were removed by filtration through 5 μ , 0.65 μ , and 0.025 μ filters. Of these solids, 88 wt% were dissolved by further treatments, 8M HNO₃ - 0.1M HF leach, NaHSO₄ fusion, and Na₂O₂-NaOH fusion. The filtered dissolver solution, and the undissolved solid solutions were analyzed by AEA and GSA. The U and Pu were extracted from the dissolver solution using 30% TBP-NPH and an 8-stage mini-centrifugal contacting unit.

The resultant solution was evaporated to dryness with the condensate collected, and the off-gas passed through a 1M NaOH trap, and an activated charcoal trap. The condensate and traps are being analyzed.

The initial AEA of the solution from the Na_2O_2 fusion of the solids collected on the 5 μ filter had given large Am, Cm, and Pu numbers; therefore, reanalysis of this sample was performed giving much lower percentages of Am, Cm, and Pu in the solids, 0.4%, 0.004%, and 0.05%, respectively. This great change in composition can be attributed to a sample mix-up. Comparison of the AEA for the filtered dissolver solution with the AEA of the Na_2O_2 fusion shows nearly identical solution compositions.

Full-Level Radioactive Glass Specimens: Glass Maker - Y. B. Katayama and C. E. Bigelow

The first batch, 100 grams, of fully radioactive glass was made by in-can melting in a 1-1/2 in. OD 304 L stainless steel crucible. A vitro-forming mixture consisting of 75 g of 73-1 frit plus 25 g of prepared waste calcine, was put into the crucible and furnace heated in an enclosed chamber to 1050°C and held at this temperature for 3 hr before furnace cooling to room temperature. The off-gases of the vitrification process were continuously purged by a carrier gas (cell air) flowing past a water-cooled platinum chill plate and through a caustic scrubber, a water scrubber and a wet-test meter. The chill plate collected 0.0406 g of condensed solids which will be chemically analyzed along with the scrubber solution.

The prepared waste calcine was made by heating the solid waste to a calcine reference temperature of 500°C for one hour in the glass melting chamber. Radiochemical composition of the volatilized products during calcining were determined from analyses of the scrubber solution. A 100 g batch of calcine had the following losses:

<u>Analyzed Radioisotopes</u>	<u>Feed Composition</u>	<u>Losses</u>
Ce 144	89 Ci	320 nCi
Ru 106	26 Ci	3800 nCi
Cs 134	60 Ci	390 nCi
Cs 137	70 Ci	520 nCi
Am 241	100 mg	2 nCi
Cm 244	30 mg	7 nCi
Cm 242	0.5 mg	4 nCi
Pu 239 + 240	80 mg	<0.07 nCi

These losses are minimal when compared to the 10% volatilized losses during the evaporation of the waste to dryness.

Fuel Level Radioactive Glass Characterization - D. J. Bradley and C. E. Bigelow

The first HLW glass canister run was cut into seven wafers. One was kept as an archive and the remaining six are being dynamically leach tested according to a procedure closely following that prepared by the IAEA.⁽²⁾ This test was begun on February 9, 1976. Leach samples of 10 ml are being acidified with 100 λ of concentrated nitric acid to prevent transuranic isotopes from plating out.

Two other HLW glass runs have been made following the same procedures of the first run. These glass canisters have also been sectioned and a dose rate reading was taken on each wafer through a port in the hot cell wall. Figure 2.8 shows the variation in dose rate with depth of glass for the three runs made to date. The curves show the stratification within the melt as evidenced by the change in dose rate.

At the present time, the following programs are being proposed and evaluated to further characterize the HLW glass:

1. Characterization of glass inhomogeneities
2. Determination of elemental leach rates from HLW glass
 - a. Static leach test
 - b. Effect of leach solution

- c. Effect of temperature
- d. Effect of surface area
- 3. Investigate leach rate interaction with geologic media.

FIGURE 2.8. Dose Rate as a Function of Depth of High Level Waste Glass

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

The purpose of this work is to determine changes in properties of high-level waste glass as functions of time and temperature.

Characterization of 72-68 glass samples through two months storage at elevated temperatures is continuing. During the quarter, density and porosity

measurements were completed. Additional X-ray and microprobe analyses of the glass are presented in the Phase Behavior section of this document.

An average density of 3.38 g/cc was measured for the 72-68 glass. No relationships between temperature, time, or porosity were evident.

Total open porosities for two month storage samples are graphed in Figure 2.9. The peak porosity occurs 50°C higher for the one week samples. The porosity is due to microcracking caused by differences in thermal expansion for Zn_2SiO_4 and the surrounding glass. X-ray diffraction measurements of Zn_2SiO_4 concentrations in the glass substantiate this correlation.

FIGURE 2.9. Total Open Porosity vs Temperature
Two Months

The differences in the porosity of the TOP, MIDDLE, and BOTTOM layers at higher temperatures are due to settling of the Zn_2SiO_4 , resulting in more microcracking in the BOTTOM section.

CANISTER CORROSION STUDIES - R. F. Maness

Canister corrosion studies are an integral part of the Waste Fixation Program, including investigations of corrosion under processing conditions and during long-term storage of candidate solidified waste forms.

Silicon metal is currently being added to calcine prior to melt formation primarily to maintain molybdenum in its lower valence states and thus inhibit the formation of a relatively soluble secondphase material. Zircaloy cladding sections could be used to serve the same purpose. A major reduction product produced by the reaction of silicon or Zircaloy with melts prepared from calcine and a zinc-bearing borosilicate glass frit appears to be zinc vapor which burns at the surface of the melt to form zinc oxide. There is, therefore, some concern regarding embrittlement of the canister when silicon or Zircaloy are added during in-can melting. Tests were made at 1050°C with 304L and a melt prepared from PW-7-2 calcine and 73-1 frit containing Zircaloy tubing sections or silicon metal (1.5 wt%, - 325 mesh). Increased general corrosion as well as the initiation of intergranular attack were noted in both cases after 48-hr exposures. However, no major loss of ductility was noted. Maximum penetration as determined by metallography was 2 to 3 mils.

An additional experiment was made in which one-inch lengths of Zry tubing were added to a glass melt held at 1050°C. The melt was prepared from PW-7-2 calcine and 73-1 frit. The tubing sections were obtained from 0.440 in. diam Zry-4 tubing. However, in this case, the tubing sections were embrittled (hydrided) to the point of near nil ductility by exposure to ferric chloride solution and then oxidized in air (about 100 mg/dm²) prior to adding to the melt. In contrast to the last experiment made with non-hydrided and water oxidized (~500°C) Zry-4, no combustible gas was produced during the 24-hr exposure period. The hydride case in the Zry-4 tubing appeared to comprise

about 50% of the wall thickness. The remainder of the Zry retained its ductility throughout the exposure.

Corrosion tests were made with 304L to determine the effect of chloride and fluoride additions to a melt prepared from PW-7-2 calcine and 73-1 frit. With chloride and fluoride additions at the 1% level (as NaCl and NaF), and with a melt temperature of 1050°C, corrosion rates were 2.1 and 17.4 mils/month, respectively. A control specimen corroded at a rate of 2.4 mils/month. Intergranular attack was evident only on the specimen exposed to the fluoride-bearing melt.

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2. Letter from J. E. Mendel, "Summary of Leach Test Round Robin I Results," February 13, 1975, Battelle-Northwest.

SECTION 3.0 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 processes will be available for containment of high-level wastes. 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. Alternative processes are now being developed on the laboratory scale.

In the concept currently being developed the waste is formed into a small granule or pellet which is coated with a nonradioactive inert material to provide containment and leach resistance. The coated waste shape is then incorporated into a metal matrix which provides impact resistance and increased thermal conductivity.

DEVELOPMENT OF COATED WASTE PARTICLES - W. J. Gray and M. F. Browning

The purpose of this study is to develop coating materials and processes which can be applied to waste particles to serve as a fission product barrier. Coating of particles typical of those produced in a fluid-bed calciner (0.1 to 1 mm), as well as particles several millimeters in diameter, is being investigated.

Several metal, oxide, and carbide coatings (a partial listing was given previously⁽¹⁾) have been applied to small (100 to 300 μm) simulated calcined waste particles at Battelle's Columbus Laboratory (BCL). The best-quality coatings, particularly in terms of high-temperature (up to 1200°C) behavior, have been pyrolytic carbon (PyC) applied at General Atomic and ORNL, as well as at BCL. Al_2O_3 coatings have also looked encouraging although the necessary quality has not yet been achieved. Current thinking is that PyC may be the best coating material in terms of leach protection but that it may be desirable to provide oxidation protection for the PyC with an overcoating of Al_2O_3 .

Recently it has become apparent that disc pelletizing is a better way to produce pellets suitable for coating than is a fluid-bed calciner. The former

produces pellets 1 mm diameter or larger while the latter produces pellets smaller than 1 mm. Therefore, BCL's attention is being directed toward the application of high-quality Al_2O_3 coatings to the larger pellets.

There are at least three coating systems that might be considered for this application: (1) Rotating-drum, (2) Fluidized-bed with particle movement enhanced by an immersed mechanical screw, and (3) Fluidized-bed with auxiliary agitation provided by mechanical vibration. The latter has been chosen for the initial studies because high-quality coatings are usually more difficult to achieve with the first two methods.

A typical fluidized-bed was supported by an assembly attached to a 3600 Hz adjustable amplitude vibrator so that the movement was parallel to the axis of the reactor (vertical). Several experimental runs have been made using either a $\sim 1200\text{ }\mu\text{m}$ PyC particle or a $\sim 2200\text{ }\mu\text{m}$ hollow carbon particle. The carbon particles were used as an expedient to establish the quality of coating resulting from various coating parameters. This was easily accomplished by heating the coated particles for several hours at 1000°C in air. The loss of carbon substrate as determined by weight and/or visual observation was a measure of the coating integrity.

Although varying degrees of protection have been provided by the coatings applied in a vibrating fluidized-bed, none has given the protection thought to be required. This conclusion is based on the results of the test described above which involved oxidation at elevated temperatures of the carbon substrate. In general, the coatings have not been of the quality typically obtained in a conventional fluidized-bed coating system, i.e., the coatings have not been as dense or as impervious. There are several explanations for obtaining poorer quality coating in a vibrating fluidized-bed system, such as (1) coating temperature lower than indicated, (2) reactant composition not that intended, (3) reactants not mixed thoroughly, (4) carbon substrate affecting the nucleation characteristics of the deposited Al_2O_3 , (5) gas flow pattern adversely affected, and (6) particle contact less frequent with lower impact. All of these factors will be considered in improving the coating quality, but numbers (3), (5), and (6) are the ones most likely responsible and will receive the initial attention.

In the future, improved pellets will be factored into the BCL coating studies. These will be produced with the disc pelletizer using supercalcine developed at Penn State. Supercalcine vaporizes to a significantly lower degree (~1 wt% in 17 hours at 1200°C) than either regular calcine or 72-68 glass. Thus higher coating temperatures can be used with less problem due to vaporization of the pellet.

METAL MATRIX - K. R. Sump and S. Begej

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.

In a literature review conducted to examine the pertinent properties of various matrix materials, it was concluded that 304 stainless steel was superior with regard to oxidation resistance and tensile strength as shown in Table 3.1. Manganese bronze was superior in resistance to corrosion in sea water, while pure iron was superior with regard to impact toughness. The thermal conductivity of 304 stainless steel was the poorest of the materials surveyed and copper was the best.

Cast Matrix

Calcine-frit spherical pellets made by the disc pelletizer were cast in a matrix of both aluminum and lead. The pellets used were ~1/4 inch diameter. The aluminum was cast at 750°C and the lead at 400°C. Some difficulty was experienced with the aluminum during pouring though the screen holding down the pellets. The lead penetrated the screen and pellet structure very well.

Gravity Sintered Matrix

A gravity sintered, copper matrix sample containing simulated 100% calcine waste particles was successfully fabricated at 940°C for ~40 hours. The pure calcine particles were 2 to 3 mm in diameter and the copper spheres were -45 + 100 mesh.

TABLE 3.1. Properties of Matrix Materials

Material	M.P. (°C)	Density (gm/cc)	Tensile Strength (kpsi)(°C)	Impact Strength Room Temperature ft#, Charpy V	Relative Thermal Conductivity (20°C)(Pure Cu=1)	Corrosion Rate in Sea Water cm/yr x 10 ⁻⁴	10,000' yr Oxidation Depth in Air (cm)(815°C)
304 SS (wrought, annealed)	2550-	7.96	95 ⁽²⁾	130	0.038	13 ^(a)	0.017 ^{(b)(3)}
Lead (cast, + 99.5%)	326	11.36	3	10	0.088	13 ⁽⁴⁾	-
Aluminum, Type 43 (sand cast) 5% Si	574- 632	2.69	19		0.36	36 ^{(c)(4)}	-
Mn Bronze Type 8A, (cast)	862- 880	8.3	70	32	0.22	3 ⁽³⁾	1.3 ^{(d)(3)}
Copper (pure)	1083	8.96	56 ^(e)	47 ^(e,f)	1.00 ^(g)	40	22.1 ⁽⁵⁾
Iron (pure)	1536	7.87	35	240 ^(h)	0.19	69 ⁽ⁱ⁾⁽⁴⁾	209 ⁽⁵⁾

Source: Reference 1, unless otherwise stated.

- (a) Alloy is prone to local failure from pitting.
- (b) Pure oxygen
- (c) Alloy 1100-H14; has susceptibility to crevice corrosion.
- (d) 60% Cu-40% Zn alloy at 800°C
- (e) DHP copper
- (f) Charpy keyhole
- (g) Thermal conductivity = 0.941 cal/cm²/cm/°C/sec
- (h) <0.11°C
- (i) Carbon steel

Brass samples with and without calcine-frit particles were fabricated at temperatures of 750-850°C. The brass powders were -100 mesh and the compositions were 55 Cu 44-3/4 Zn 1/4 Mn and 58-1/2 Cu 40 Zn 1-1/2 Pb. The desired manganese bronze powder has not been located.

PELLET FORMING METHODS - A. A. Garrett

The objective of this task is to evaluate the disc pelletizer as a possible means of pelletizing calcined waste prior to coating with an inert material. The main purposes are to determine if a disc pelletizer can make high density, uniform spheres from a mixture of calcine and frit and to determine the feasibility of operating a disc pelletizer in a hot cell.

Fifteen kg of Supercalcine⁽⁶⁾ produced in BNW's spray calciner were successfully pelletized in a disc pelletizer. The resulting sintered cores (pellets) ranged in size from 1 to 3 mm in diameter. The "natural" core size (size most easily formed) for this particular material is around 2.7 mm.

Different batches of the core were sintered at 1000, 1100, 1150, 1175, and 1200°C for 3 hours to determine the optimum sintering temperatures. The cores fired below 1175°C were fragile and yielded low densities while those fired at 1200°C were quite rugged and yielded densities around 3.7. The supercalcine feed used here gives a waste loading of about 50 wt%.

Cores sintered at 1200°C were examined using a scanning electron microscope. Figure 3.1 shows the relatively smooth surface of a 1.5 mm supercalcine core. The smooth surface greatly facilitates coating in a CVD fluidized-bed.

FIGURE 3.1. Supercalcine Core Sintered at 1200°C - 40X

Figure 3.2 shows the surface of a 1.5 mm diameter core magnified 10,000 times. The photo illustrates the crystalline nature of the supercalcine waste product.

FIGURE 3.2. Supercalcine Core Sintered at 1200°C - 10,000X

ADVANCED WASTE FORMS RESEARCH AND DEVELOPMENT (PENNSYLVANIA STATE UNIVERSITY)

G. J. McCarthy

The objective is to develop a waste form in which all of the radioactive atoms will be isolated in thermally and chemically stable phases. If adequately consolidated, this waste form might stand alone; but it is also being considered as the innermost barrier in a multiple layer optimum waste form. Because this waste form utilizes the existing calcining processes with a compositionally modified waste liquid it has been termed "supercalcine". Near term objectives are: 1) to determine the best crystalline phases for Cs, Ru and Te fixation, 2) to develop "supercalcine" formulations containing all major commercial waste atoms and 3) develop means of consolidating the crystallized product.

Supercalcine Crystal Chemistry - G. J. McCarthy, C. A. Smith, M. T. Davidson,
and D. E. Pfoertsch

To date, identification of the structures and approximate compositions of the phases in crystallized supercalcine has been accomplished through careful studies of x-ray diffractograms. Compositional--microstructural analyses by Scanning Electron Microscopy which will add further chemical information are in progress. The best confirmation of a proper x-ray identification in a complex mixture is to prepare the pure phase of the proposed stoichiometry, confirm that a single phase has been formed and match its diffractogram to a set of reflections in the supercalcine diffractograms. These steps have been carried out from the beginning of this project, but were given special emphasis during the last quarter. The following stoichiometries were selected to approximate the proposed compositions of phases identified in crystallized supercalcine and described in the preceding quarterly report.⁽⁷⁾

Each of these stoichiometries gave well-crystallized single phases of the specified structure type when prepared according to the same calcining and firing schedules as supercalcine. The comparison of diffractograms of these phases to those of crystallized supercalcine confirmed the phase assignments made earlier. Unit cell parameters and complete x-ray powder data have been determined for each phase and are available from the author.

* BNWL 1994.

** The A_{ss} and P compositions expected from PW-7 based supercalcine formations; K is a stand-in for Rb. All other phases are based on PW-4b waste.

When simple waste calcine is fired, the dominant crystalline phase is a fluorite structure solid solution (F_{ss}) obviously rich in CeO_2 . It was puzzling that when only 30 wt% of additives are combined with the wastes to produce supercalcine the F_{ss} phase is weak or absent in the diffractograms of the crystallized product. Compatibility studies confirmed that CeO_2 does not react with any of the well established phases in supercalcine. The explanation may be in the excess SiO_2 which is included in every supercalcine formulation to insure Cs fixation as $CsAlSi_2O_6$. Perhaps the Ce was reacting with this SiO_2 to form an apatite structure phase which would be incorporated in solid solution with the "tailor-made" apatite phase.

A series of Ce silicate apatite models including various proportions of Ca, Sr and Nd were tested. It was found that if Ca were the alkaline earth then Ce could completely replace Nd in the model $Ca_{2+x}Nd_{8-2x}Ce_x[SiO_4]_6O_{2-\frac{x}{2}} \square \frac{x}{2}$,* i.e., x can have any value from 0 to 4. When Sr replaces Ca, less Ce can replace Nd. For $x = 2$ or more, other phases (e.g. $SrSiO_3$, CeO_2) are formed in addition to an unknown apatite stoichiometry. However, $Sr_3Nd_6Ce[SiO_4]_6O_{2-y}^{**}(x=1)$ gives the approximate Ce/RE ratio in PW-4b and both excess Sr and SiO_2 were added in supercalcine 75-2. Therefore, these crystal chemical results imply that future supercalcine formulations should specify Ce in the A_{ss} rather than an F_{ss} phase. This has also been demonstrated in several of the compatibility studies described below.

In all of our phase formation models we have assumed, based on ample literature data, that the phosphate present in the wastes will substitute for the $[SiO_4]$ groups in A_{ss} . The correctness of this assumption was confirmed through preparation of a number of A_{ss} phases containing either Sr or Ca with the rare earth and phosphate concentrations found in PW-4b and PW-7 wastes. Two of these compositions were listed in the A_{ss} group at the beginning of this section.

* The products were black, indicating some amount of reduction of Ce^{4+} to Ce^{3+} --this model assumes complete reduction to Ce^{3+} . Experiments designed to establish the actual valence of Ce in these phases are in progress.

** y will vary from 0 to 0.5 depending on the valence of Ce.

Compatibility Studies (G. J. McCarthy and M. T. Davidson)

Sixteen complex assemblages of oxides were studied to gain further insight into the phase formation in crystallized supercalcine, especially where excess Al and Si have been added. Highlights of the results follow.

- The role of Ce described in the previous section was confirmed through a series of increasingly more complex assemblages of constituent oxides to which excess SiO_2 had been added. The Ce acts as a typical RE^{3+} and, combined with the required proportion of the excess SiO_2 , substitutes into the A_{SS} phase.
- The compatibility of the tetragonal phase of ZrO_2 (T_{SS}), probably containing some CeO_2 or CaO in solid solution, with other supercalcine phases was confirmed.
- It had been repeatedly noted that the reflections of the S_{SS} phase $(\text{Sr}, \text{Ba}, \text{Ca})\text{MoO}_4$ grow weaker in diffractograms of supercalcine with extended firing above 1100°C . Several runs indicated that this may be due in part to replacement of some Sr by Ca in S_{SS} . It appears that the Sr has a stronger tendency to form aluminosilicates. The x-ray intensity of CaMoO_4 is less than an equimolar amount of SrMoO_4 .

Supercalcine Development (G. J. McCarthy and D. E. Pfoertsch)

Consolidation. The engineering scale preparation of a fine powder spray supercalcine (using a simplified PW-4b waste) at PNL has been demonstrated. The next step in establishing the feasibility and desirability of including supercalcine as the first barrier of a multi-barrier alternative waste form is consolidation of the powder into coarse grains or pellets.

We are utilizing simple cold pressing for pellet forming followed by firing at 1100 - 1200°C for crystallization-sintering. Recently, we found that adding small amounts (2-12 wt%) of Corning code 7740 ("Pyrex") glass frit to the supercalcine gave much improved consolidation and very good leaching resistance and thermal stability. A typical set of processing conditions and properties follows.

90% Spray Supercalcine 75-2 (60% waste loading)

10% 7740 frit, -200 mesh

pressed into 1/2 in. pellets at 25,000 psi

fired at 1100°C for 1 hr

soxhlet leachability:

% weight loss after 1 day: 0.41

3 days: 0.84, 1.1, 0.55

thermal stability (-200 mesh powder)

% weight lost after 1 day at 1200°C: 1.5%

2 days at 1200°C: 3.2%

3 weeks at 1200°C: 6.2%

3 weeks at 1050°C: 4.3%

3 weeks at 900°C: 1.2%

The soxhlet weight loss values are comparable to those observed for the better glass waste forms which have only half this level of waste loading. The weight losses* of the powdered product are higher than desired but still quite reasonable when it is considered that the oxides of Cs, Mo, B, Na and K** make up ~18 wt% of the product oxide components. It should be noted that previously formed pellets showed no detectable weight losses during one hour's firing at 1050°C. This indicates that supercalcine pellets could have coatings applied at this temperature without fear of significant waste volatilization.

As we have previously reported, hot pressing is the optimum consolidation technique for oxide powders such as supercalcine. To see how much improvement could be obtained with this method, we had pure supercalcine 75-2 vacuum hot pressed at the same crystallization temperature we had used in air firings. The conditions were 15 min at 1100°C and 3000 psi in a 2-in. graphite reactor. The product was very hard and dense and could be polished to a mirror finish. It had a 3-day soxhlet weight loss of 0.49%

* We have reason to believe that some of these losses may be due to slow release of H₂O previously incorporated in the A_{ss} phase as (OH) on the halide site.

** In BNWL-1932, Gray finds that these are the most readily volatilizable species.

even though the level of waste loading was 68%. If hot pressing can be developed for remote operation under high flux conditions, it will be the process of choice for supercalcine consolidation.

PW-7 Based Formulations. PW-7 differs from PW-4b in having significantly higher RE^{3+} (Gd), Fe, $[PO_4]$ and U concentrations plus a small amount of Na. Since we feel that the crystal chemical roles of these constituents are substantially (though not completely) understood, our current supercalcine phase formation models were also applied to this waste formulation.* The x-ray diffractograms of the crystallized product were consistent with the phase formation model and showed only a few weak unidentified reflections. According to the model, Gd and $[PO_4]$ were incorporated in A_{SS} , Na in pollucite, U in an F_{SS} phase and Fe remained as the oxide. Evidence of volatilization of Cs and other waste species at 1100°C (stained bricks, frosted silica tubes) was absent for the formulation where twice the (Al+Si) required for pollucite $[(Cs,K,Na)AlSi_2O_6]$ formation was added. Experience has indicated that in actual spray calcine preparation, where the complex oxide mixtures will have far greater homogeneity, this level of excess (Al+Si) will not be necessary.

When the alkaline earth (Ca and Sr) additive concentration was increased by a factor of 1.25 above that called for in the phase formation model, there was evidence of some Cs volatilization during the crystallization heat treatment. Apparently the Sr or Ca ties-up some Al and or Si and prevents full crystallization of pollucite. This sensitivity to excesses of either waste constituents or additives is not desirable. We currently suspect that the A_{SS} model used may be calling for too much additive Ca, so we will continue to concentrate our crystal chemical and compatibility studies on this important supercalcine phase.

* Only Ru, Te, Ag and the radioactive species were not included in our simulated waste.

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SECTION 4.0 SYSTEMS SAFETY EVALUATION

The purpose of the Systems Safety Evaluation Task is to define and investigate waste management systems in relation to the containment, immobilization, and isolation of the wastes and to evaluate the risk and cost implications of these systems. Currently, the likelihood and consequences (risk) of potential release incidents are being estimated for a reference system for the management of high-level waste that includes liquid storage through retrievable surface storage operations.

FAULT TREE EVALUATION METHODOLOGY - T. H. Smith, P. J. Pelto, D. L. Stevens, G. D. Seybold, W. L. Purcell, and L. V. Kimmel

The objective of this effort is to develop a suitable automated methodology for evaluating large fault trees representative of complex waste management facilities and operations. The approach is to develop a computer code system capable of importance-screening very large numbers of failure sequences (cut sets). The screening is to be based on a crude measure of risk rather than on probability or consequences individually. Cut sets identified as constituting the dominant risk will be retained for more detailed analysis.

A report was published⁽¹⁾ describing the risk-based fault tree analysis method developed for the identification, screening, and preliminary evaluation of potential release sequences of the reference system (Figure 4.1).

RISK ASSESSMENT - L. V. Kimmel, E. S. Murphy, P. J. Pelto, T. H. Smith, J. M. Taylor, and W. K. Winegardner

The objective of this effort is to assess the risk associated with the liquid storage, liquid transfer, solidification, water basin storage, transportation, "offsite" retrievable surface storage and solids handling activities of the reference system. Fault trees are being used to identify potential failure events, i.e., events that could conceivably result in release of radionuclides from containment/confinement barriers.

FIGURE 4.1 Reference High-Level Waste Management System
(Levels of Activity and Accumulations Estimated for Year 2000)

Using the techniques described in Reference 1, dominant failure sequences for the accidental release of radionuclides have been tentatively identified for the various activities of the reference system. Dominant sequences were identified as those with the highest mathematical product of probability and consequences, the latter in terms of quantities of waste released. The initial assessment revealed that dominant scenarios that could conceivably have significant public health and safety impact are highly improbable, e.g., one accidental release per million years or less.

Accidental releases of radioactive material initiated by both process operating events and plant external events, (e.g., earthquake or impact of a giant meteor) were found to contribute to total system risk. Except for the operating induced interruption of cooling water to stored liquid and solidified waste, postulated release scenarios contributing the bulk of the risk for the various waste management operations involved sequences initiated by external events.

Dominant scenarios with conceivable significant public health and safety impact were associated with the passive storage activities rather than the relatively active modes of solidification and transportation. This appears to be primarily the result of the massive inventories associated with the passive storage activities rather than the populations and climatology assumed or the age (radioactivity) of the waste during a particular activity. Dominant scenarios were associated with airborne rather than surface or ground water pathways.

Reevaluation of this initial assessment is now needed to assure that insights obtained by comparisons are valid. Sequences identified as constituting the dominant risk need to be subjected to detailed analysis. Review of significant input data and sensitivity studies are needed along with efforts directed at establishing error bounds and uniformity concerning assumptions.

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