Multibarrier Waste Forms Part II: Characterization and Evaluation

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August 1979

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

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

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PACIFIC NORTHWEST LABORATORY
operated by
BATTELLE
for the
UNITED STATES DEPARTMENT OF ENERGY
Under Contract EY-76-C-06-1830

Printed in the United States of America
Available from
National Technical Information Service
United States Department of Commerce
5285 Port Royal Road
Springfield, Virginia 22151

Price: Printed Copy \$____*; Microfiche \$3.00

*Pages	NTIS Selling Price
001-025	\$4.00
026-050	\$4.50
051-075	\$5.25
076-100	\$6.00
101-125	\$6.50
126-150	\$7.25
151-175	\$8.00
176-200	\$9.00
201-225	\$9.25
226-250	\$9.50
251-275	\$10.75
276-300	\$11.00

3 3679 00049 3215

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SUMMARY

The multibarrier concept for the storage of radioactive waste is to use up to three barriers to isolate radionuclides from the environment: a solidified waste inner core, an impervious coating, and a metal matrix. The coating and metal matrix give the composite waste form enhanced inertness with improvements in thermal stability, mechanical strength, and leach resistance. Multibarrier Waste Forms Part I: Development describes research and development that resulted in one-liter demonstrations of four multibarrier waste forms for nonradioactive, simulated waste compositions.⁽¹⁾

The four multibarrier waste forms were evaluated for thermal stability (volatility), mechanical strength (impact resistance), and leach resistance. This report discusses the characterization of the multibarrier waste forms and compares them to reference calcine and glass waste forms. The results of these multibarrier characterization studies can be summarized as follows:

- The weight loss of supercalcine-ceramics after 4 hr in dry air ranges between 0.01 and 1.6 wt% from 1000 to 1200°C and is dependent upon composition.
- Glass Marbles in a cast lead alloy offer approximately an order of magnitude decrease in the wt% fines <37 µm released after impact as compared to a glass monolith. CVD-coated supercalcine in a sintered 410 SS matrix offers up to two orders of magnitude decrease.
- Hot-pressed supercalcine ceramics may offer no increase in impact resistance or leach resistance over that of a glass monolith.
- Supercalcine may offer no advantage over waste glasses in leach resistance.
- Glass and PyC/Al₂O₃ coatings provide effective inert leaching barriers.

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MULTIBARRIER WASTE FORMS
PART II: CHARACTERIZATION AND EVALUATION

INTRODUCTION

The High Level Waste Immobilization Program conducted by the Pacific Northwest Laboratory (PNL) for the United States Department of Energy (DOE) has the objective to develop processes for converting High Level Liquid Waste (HLLW) from alternative fuel cycles to solid forms demonstrated to be physically, chemically, and radiolytically stable and inert. A major part of this program has been in-depth studies on low-melting (1000-1150°C) borosilicate glasses.^(2,3) These borosilicate glasses have become the "reference" waste form at PNL.

In 1973 a parallel but much smaller task than the glass studies was initiated to develop advanced waste forms or waste form alternatives to the reference glass systems. The primary emphasis of this multidisciplinary task has been to develop waste forms based upon a multibarrier concept as illustrated in Figure 1. The multibarrier concept is to create barriers between the radionuclide-containing inner core material and the environment by the use of coatings and metal matrices. The resultant composite waste form exhibits enhanced inertness from improved thermal stability, mechanical strength, and leachability.

The feasibility of producing lab-scale multibarrier waste forms was demonstrated by the encapsulation of one-liter volumes of simulated waste glass marbles and coated and uncoated supercalcine.⁽⁴⁾ Based on the development work for these waste forms, recommendations have been suggested for further development of various processes involved in realizing the multibarrier concept.⁽¹⁾

Following lab-scale demonstration of the multibarrier concept, an evaluation of the waste forms must consider both the level of inertness achieved (risk analysis) and the process engineering of producing the waste forms in a

FIGURE 1. Multibarrier Concept for Isolating Nuclear Waste

full-scale operation. As the required level of inertness or stability increases, the technological complexity of the processes would generally be expected to increase, approaching the limits of engineering feasibility. This general trend, suggested by Figure 2, has not been characterized in sufficient detail to identify an optimum tradeoff between waste form stability and complexity.

The reference waste glass system (monolith) has been compared to unconsolidated calcine with respect to levels of achieved inertness.⁽⁵⁾ Two "high-risk" scenarios, high-velocity impact and high-temperature excursions, were considered with waste form inertness characterized by ratios of waste dispersion by water (leachability), by air (impact or frangability) and by high temperature (volatility). Waste dispersion by water was considered not to be a high-risk scenario. Potential differences in release rates between unconsolidated calcine and the reference waste glass are shown in Figure 3. The reference waste glass offers almost 100 times less dispersion by air than the calcine and ~10 times less dispersion by high-temperature excursions at 1200°C. It will be shown in this report that multibarrier products may be even orders of magnitude better than calcine or glass in these areas of inertness.

With this concept of risk analysis in mind, the multibarrier waste form was characterized in this program to obtain data on bulk properties, thermal

FIGURE 2. Stability of Waste Forms Versus the Technological Complexity of Producing the Waste Forms

stability, leachability, and impact resistance. This included tests on lab-scale samples of encapsulated and unencapsulated inner core materials leading up to the selection of materials for the one-liter demonstrations. Although characterization of the multibarrier waste forms will be incomplete until the one-liter multibarrier samples are fully characterized, these "preliminary" characterizations can be used to recommend further direction of multibarrier waste form development. A brief study of the effects of radiation on the multibarrier waste forms was also conducted.

A study of process considerations was conducted to evaluate the complexity of scaling up the proposed multibarrier processes. The study considered volume capacity, waste loading, and heat distribution.

FIGURE 3. Potential Differences in Release of Calcine and Glass⁽⁵⁾

CHARACTERIZATION OF THE MULTIBARRIER WASTE-FORMS

BULK PROPERTIES

Table 1 presents a summary of the pertinent bulk properties of multi-barrier waste forms. Details on supercalcine and glass marble fabrication, along with PyC/Al₂O₃ and glass coating techniques, can be found in Multi-barrier Waste Forms Part I: Development.⁽¹⁾ Densities and porosities of these waste forms have been reported with the development work.⁽⁴⁾ Thermal conductivity measurements were determined using the comparative method. The "maximum use temperature" reported for the different multibarrier waste forms is based on either melting points or temperatures at which reactions occur between multibarrier components.

THERMAL STABILITY

Thermal stability was considered with regard to

- 1) process considerations - possible reactions that may occur during the forming and/or encapsulation processes,
- 2) the effects of high-temperature heat treatment on coated inner cores and the encapsulated product, and
- 3) the volatility of the supercalcine inner core being considered as a component of the multibarrier waste form.

Process Considerations

Several core-matrix combinations have been tested as outlined in Table 2. Examples of encapsulated cores are illustrated in Figure 4. In general, encapsulated products showed a gap between the core and the matrix. Some penetration into the core was observed for uncoated supercalcine cast in Pb-10Sn.

Reactions between the inner core and the matrix during encapsulation were only observed for uncoated supercalcine in gravity-sintered 316 stainless steel (SS). Scanning electron microscope analysis (SEM) detected no reactions for uncoated supercalcine encapsulated in vacuum-cast Pb-10Sn and

TABLE 1. Bulk Properties of Multibarrier Waste Forms

Inner Core	Coating	Matrix	Encapsulation Method	Bulk Density, g/cm ³	Thermal Conductivity, (a) W/m-K	Maximum Use Temperature, °C
ICM-11 Waste Glass	none	none	--	3.4	0.84	550
ICM-11 Waste Glass Marble	none	Pb-10Sn	Vacuum Cast 400°C	6.2	8.3	250
Supercalcine SPC-2 ^(b)	none	none	--	4.88	0.91	1200
Supercalcine SPC-4 ^(c)	none	none	--	4.03	N.D. ^(d)	1200
Supercalcine SPC-2 ^(c)	none	none	--	2.35	N.D.	1200
Supercalcine SPC-4	none	Al-12Si	Vacuum Cast 650°C	3.5	51.0	550
Supercalcine SPC-4	Glass (~1 mm)	none	--	3.66	N.D.	600
Supercalcine SPC-4	Glass (~1 mm)	Al-12Si	Vacuum Cast 650°C	3.4	45.0	550
Supercalcine SPC-2	PyC (40 µm) Al ₂ O ₃ (60 µm)	none	--	2.5	N.D.	1200
Supercalcine SPC-2	PyC (40 µm) Al ₂ O ₃ (60 µm)	Cu	Gravity Sintered 900°C - 8 hr	3.48	24.0	1000

(a) Determined by comparative method at 200°C

(b) Hot pressed

(c) Disc pelletized

(d) Not determined

TABLE 2. Inner Core-Matrix Combinations Fabricated for Characterization

Matrix Materials	Multibarrier Inner Core Materials			
	Simulated Waste Glass Marbles	Supercalcine		
		Uncoated	Glass-Coated	Al_2O_3 -Coated PyC/ Al_2O_3 -Coated
Vacuum-Cast Metals				
Al-12Si	•	•	•	
Lead	•			
Pb-10Sn	•	•		
Pb-5Sn	•			
Gravity-Sintered Metals				
Copper		•		•
Stainless Steel		•		•

FIGURE 4. Encapsulated Inner Cores

Al-12Si and gravity-sintered Cu. The bonding between Cu spheres in the gravity-sintered Cu sample was minimal. Very little growth between particles was observed, as illustrated in Figure 5. Flux coating is being investigated to improve the bonding.

The gravity-sintered 316 SS sample had a reaction zone around the SS particles as shown in Figure 6. Energy dispersive X-ray analyses of the white area (labeled A) and the darker crystalline area (labeled B) were conducted. The white area has high Mo, Cr, and Fe contents, whereas the darker crystalline region surrounding the SS particle is primarily Cr. Samples of coated supercalcine encapsulated in gravity-sintered 316 SS do not contain any of the above observed phases. This, along with vaporization studies that show that a considerable amount of Mo is vaporized, leads to the conclusion that the observed reaction products may be caused by supercalcine vaporization. If supercalcine is to be encapsulated at higher temperatures a coating may be necessary.

High-Temperature Heat Treatment of Coated Inner Cores

In the initial chemical vapor deposition (CVD) coating studies, both supercalcine and a calcine-frit^(a) mixture were used as substrate materials and coated with 33-39 μm of Al_2O_3 . The coatings were applied at 825°C and 1025°C for the calcine-frit and supercalcine, respectively.

Both samples were heat treated in an air atmosphere at 900°C for 72 hr. After 24 hr at 900°C, approximately 10% of the coating on the calcine-frit substrate cracked or displayed a reaction between the core and coating; after 72 hr over 90% of the coatings on the calcine-frit had failed. The coating on the supercalcine substrate was unaffected.

Heat treatment at 1050°C resulted in complete failure of the coatings on the calcine-frit substrate after 2 hr whereas only 5% of the coatings on the supercalcine substrates cracked. The failure of the coatings on the calcine-frit substrate appeared to be caused by a reaction in the coating. By use of

(a) PW-4a and 73-1 Frit

FIGURE 5. Uncoated Supercalcine Cores Encapsulated in Gravity-Sintered Cu

FIGURE 6. Uncoated Supercalcine Cores Encapsulated in Gravity-Sintered 316 SS

energy dispersive X-ray analyses (EDAX) ZnO was found to be a major component of the reaction zone. Since the frit contains ~28.9% ZnO, it was concluded that only supercalcine substrates should be used.

No apparent reactions between the PyC coating and supercalcine have been observed by optical microscopy or SEM analysis although X-ray diffraction results indicate possible formation of Mo_2C and the solid solution phase $(\text{Sr},\text{Ba})\text{C}_2$ as well as an absence of scheelite reflections.⁽⁶⁾ The PyC coating will oxidize upon heat treatment without the protection of the Al_2O_3 coating. Supercalcine cores CVD-coated with ~32 μm PyC and ~50 μm Al_2O_3 have lost only 0.16 wt% after heat treatment at 750°C for 27 hr. Complete loss of PyC coating would have given a weight change of ~2.8%.

Since the melting point of the alloys used in encapsulation of glass marbles limits the maximum use temperature, reactions were evaluated at temperatures of 500°C and less. Reactions between ICM-11 glass, Pb, Pb-10Sn, and Al-12Si were studied. The composition of ICM-11 glass is given in Table 3.

Glass-matrix reactions were not observed for Al-12Si and Pb-10Sn matrices after heat treatment for 10 days at 300 and 500°C. Above 300°C Pb-10Sn exists as a liquid; thus the 500°C sample was contained in an aluminum crucible sealed off with castable cement. The Pb-10Sn sample treated at 500°C contained a phase that appeared to nucleate from the glass marbles. From EDAX analysis it was determined that phases of Sn and Sn-Cu had precipitated out of the Pb-10Sn alloy. No elements from the waste glass were observed in the matrix.

When liquid Pb-10Sn is cooled from above 300°C, Pb crystallizes from the Pb-Sn liquid until the eutectic at 183°C is reached. Below 183°C crystalline Sn, Pb, and Sn-Pb phases can exist. Thus, the reaction area is not characteristic of the heat treatment but is formed during the cooling of the sample. The other samples did not form the Sn precipitate since their heat contents were less than that of the 500°C sample and they experienced a much faster cooling rate.

Reactions zones were observed for the Pb-encapsulated samples after heat treatment for 10 days at 300°C and 500°C. At 300°C the reaction zone appears

TABLE 3. ICM-II Waste-Glass Composition

<u>Component</u>	<u>Concentration, wt%</u>
SiO ₂	24.67
B ₂ O ₃	10.07
Na ₂ O	3.73
K ₂ O	4.33
ZnO	19.27
CaO	1.33
MgO	1.33
SrO	1.95
ZrO ₂	2.88
MoO ₃	3.70
AgO	--
CdO	0.06
TeO ₂	0.42
BaO	2.24
Fe ₂ O ₃	2.80
Cr ₂ O ₃	0.20
NiO	0.61
P ₂ O ₅	1.56
Co ₃ O ₄	0.18
Rare earth oxides	18.62

to be in the Pb matrix as illustrated in Figure 7. The dark band between the matrix and the marble is the shrinkage void.

The reaction zone observed in the sample heat treated at 300°C was identified by EDAX analysis as containing only Pb. As there is a 40-μm gap between the marble and the matrix, the reaction zone is probably an oxide of Pb. At 500°C the Pb matrix is molten and the reaction occurs as a continuum between the Pb matrix, and the glass marble as shown in Figure 7. At least two phases were observed in EDAX analysis. A needle-like phase had a high Zn and Pb content along with trace amounts of rare earths. Another separate phase area

300°C
10 DAYS

500°C
10 DAYS

FIGURE 7. Heat-Treated Waste Glass Marbles Encapsulated in Lead

had high Pb content (probably lead oxide). The rest of the reaction zone contains both Pb and elements contained in the glass.

Previous experiments had shown that molten Pb would react with waste glass. The above results only confirmed that a Pb-10Sn alloy is optimum for ICM-11 type waste glass. Even while molten at 500°C, a Pb-10Sn will not react with ICM-11 waste glass.

Reactions between uncoated supercalcine and vacuum-cast Al-12Si and Pb-10Sn matrices are not expected at temperatures below 500°C. Heat treatment experiments have not been completed on these waste forms.

Volatility Studies and Vaporization of Supercalcine

The volatility of waste calcine and zinc borosilicate glasses containing simulated HLLW has been well documented.⁽⁷⁾ Previous studies of other waste materials have been reported as listed in Table 4.⁽⁸⁾

TABLE 4. Weight Loss of Waste Materials After
12 hr at 1200°C in Dry Air

<u>Material^(a)</u>	<u>Weight Loss, %</u>
CsAlSiO ₄	0.24
CsAlSi ₂ O ₆ (Pollucite)	0.43
(Cs _{0.74} Na _{0.13} K _{0.13})AlSi ₂ O ₆	0.43
Supercalcine SPC-2	0.86
Supercalcine SPC-2 + 10% Pyrex	1.11
72-68 Glass	8.25

(a) All materials except the glass were hot-pressed pellets.

Initial volatility studies on supercalcine of the SPC-2 formulation were conducted on powder samples of spray-calcined material. Figure 8 shows weight-loss data for supercalcine SPC-2 in dry air. This material was pre-heat treated at >800°C for ~2 hours to drive off water and nitrogen oxides.

FIGURE 8. Volatility Weight Losses of Supercalcine SPC-2 Powder Versus Time

Nevertheless, it still lost 0.36% very quickly when heated at 900°C, and this was assumed to be additional water and nitrogen oxides. The vaporization studies used a platinum crucible 5/8 in. ID by 1/2 in. high (~1.6 cm x 1.3 cm). Although the crucible was filled nearly full of powder for each run, the powder sintered into a hard pellet ~0.4 in. diameter x ~0.22 in. high (~1.0 cm x ~0.56 cm) at all temperatures studied (1100-1300°C).

Preliminary data on supercalcine powder was possibly influenced by the degree of sintering. Future work, therefore, was done on pressed and sintered pellets so that the surface areas were the same in all cases.

Supercalcine pellets 1.47 cm diameter x 0.37 cm high weighing 2.0 g were prepared by cold pressing and sintering for 1 hr at 1100°C, during which time they lost <1 mg in weight. The oxide composition of the SPC-2 super-calcine is given in Table 5. Volatility measurements on these pellets were conducted using equipment described earlier.⁽⁷⁾ The pellets were held in a platinum pan, which was slightly deeper than the diameter of the pellets used in these studies.

TABLE 5. Oxide Composition of Supercalcine SPC-2

<u>Oxide</u>	<u>Composition, wt% Oxide</u>
<u>Waste Stream Constituents</u>	
BaO	2.4
CdO	0.2
Cr ₂ O ₃	0.5
Cs ₂ O	4.5
Fe ₂ O ₃	4.7
MoO ₃	8.0
Na ₂ O	0.2
NiO	0.2
P ₂ O ₅	4.2
Rb ₂ O	0.5
RuO ₂	0.5
SrO	1.6
ZrO ₂	7.6
CeO ₂	16.3
La ₂ O ₃	9.0
Nd ₂ O ₃	6.1
Pr ₆ O ₁₁	1.8
Y ₂ O ₃	0.1
Sm ₂ O ₃	1.1
Gd ₂ O ₃	0.7
Ho ₂ O ₃	0.1
<u>Supercalcine Additives</u>	
CaO	4.9
SrO	1.2
Al ₂ O ₃	4.4
SiO ₂	19.0

Gross weight-loss data for SPC-2 pellets are shown in Figure 9. The data are more scattered than has been found for other waste forms. Perhaps slight variations in density or surface area for the different pellets are responsible. The anomalously low points at 1150°C and 24 hours are reproducible, and these pellets came out a different color than at either higher or lower temperatures. Apparently the formation or decomposition of some phase occurs after long time periods over a narrow temperature range, resulting in lower volatility. X-ray characterization and SEM analysis of pellets treated in the 1100-1200°C range indicate that a primary coating of SrMoO_4 plus some apatite crystals are formed.

Chemical analyses have been run on vapor samples collected in the range 1050-1250°C after 4 and 12 hr. The 4-hr results are shown in Table 6 together with results for 72-68 glass, which were published earlier.⁽⁷⁾ The table should be interpreted as follows.

- The 72-68 data are interpolated or extrapolated values from the earlier report.
- As a result of extrapolating the 72-68 data to 1250°C, together with some conservative assumptions made in data treatment, percentage weight-loss derived exceeds 100% for Te and for Cs. Nevertheless, since the data were treated the same, comparisons between 72-68 and SPC-2 should be legitimate.
- The 72-68 data are averages of duplicate runs whereas the SPC-2 data are from only one run. The latter, therefore, should be considered less reliable.
- Gross weight loss for the supercalcine is about a factor of five less than for the glass, and the data shown here indicate that Cs vaporization from supercalcine is less than from the glass by an even larger factor (~30% less).
- Reasons for the anomalously low gross weight-loss results at 1150°C are not apparent from the data shown here. Ru loss at 1150°C is quite low, but it is a minor vapor constituent. The 12-hr analytical data (not shown) were similar to the 4-hr data.

FIGURE 9. Weight Loss of Supercalcine SPC-2 Pellets in Dry Air

Preliminary weight-loss data for supercalcine pellets of the formulation SPC-4 are given in Figures 10 and 11. These pellets (1.3 cm diameter x 0.52 cm high, weight 2.8 g) had all been prefired for 1 hr at 1200°C during which time they lost 31 mg of weight. The composition of the SPC-4 supercalcine is given in Table 7. Evidently some change occurs at temperatures above 1200°C that reduces weight-loss rates, particularly for long times. Supercalcine SPC-4 has a higher rate of weight loss above 1150°C than SPC-2 but a lower rate below 1150°C. Chemical analyses have not been run on vapor samples collected in the range 1100 to 1200°C after 4 hr and for the 1-hr prefiring at 1200°C. These results are shown on Tables 8 and 9,

TABLE 6. Weight Loss of 72-68 Glass and Supercalcine SPC-2 Pellets After Sintering for 4 hr in Dry Air

Element	Weight Loss at 1050°C				Weight Loss at 1150°C				Weight Loss at 1250°C			
	72-68 ^(a)		SPC-2 ^(b)		72-68		SPC-2		72-68		SPC-2	
	^(c)		^(d)									
	mg	%	mg	%	mg	%	mg	%	mg	%	mg	%
B	0.534	0.76	(e)	(e)	2.46	3.50	(e)	(e)	9.20	13.1	(e)	(e)
Na	0.310	0.51	0.0439	1.16	1.36	2.23	0.118	3.11	4.88	8.00	0.576	15.2
K	1.40	2.04	(e)	(e)	6.34	9.23	(e)	(e)	23.2	33.8	(e)	(e)
Rb	0.168	3.98	0.0372	0.26	0.88	20.9	0.105	0.74	3.76	89.1	0.774	5.59
Mo	0.248	0.43	0.518	0.34	1.16	2.03	2.32	1.53	4.46	7.80	9.525	6.27
Ru	0.110	0.37	0.156	1.56	0.48	1.61	0.057	0.57	4.20	14.1	0.259	2.59
Cd	(f)	(f)	0.393	10.3	(f)	(f)	0.568	14.9	(f)	(f)	0.511	13.4
Te	0.82	10.7	(e)	(e)	2.78	36.2	(e)	(e)	8.00	104.2	(e)	(e)
Cs	4.06	11.3	0.322	0.29	19.2	53.3	1.79	1.59	73.0	202.6	9.48	8.40

(a) All 72-68 glass samples referred to in this table were 2.0 g with 2.0 cm² of exposed surface area.

(b) All supercalcines pellets referred to in this table were 2.0 g with 3.4 cm² of exposed surface area.

(c) Milligram (mg) weight losses in this table refer to absolute weight losses.

(d) Percent weight losses in this table are based on the amount of the element originally present.

(e) Element not present.

(f) Element not detected.

FIGURE 10. Volatility Weight Losses of Supercalcine SPC-4 Powder

respectively. The results are typical of those obtained for vapor collected from SPC-2. It should be noted that approximately 25% of the Ru was lost during the initial 1-hr sintering at 1200°C.

LEACHABILITY

Several leachability tests are available for determination of leach resistance. A common test for scoping determinations is the Soxhlet apparatus, which is an accelerated test conducted at 95°C for normally 72 hr. Other tests commonly used at PNL for leach resistance evaluation are conducted at ambient temperatures with buffer solutions of pH 9.0 and pH 3.9. Typical values for leachability of various simulated waste glasses are given in Table 10.

The reference Pyrex glass^(a) and conventional soda-lime plate glass have Soxhlet leachabilities of 7.05×10^{-6} and 2.04×10^{-4} g/cm₂-d, respectively.

(a) Corning Code 7740.

FIGURE 11. Weight Loss of Supercalcine SPC-4 Pellets in Dry Air

Selected phases were synthesized or otherwise obtained and tested for leaching resistance to provide insight into the best candidates for the solid solutions of crystalline waste forms. Table 11 lists the compositions and structure types of those phases on which leachability results were obtained.

Supercalcine and calcine-frit substrates CVD coated with 33-39 μm of Al_2O_3 were leach-tested by the Soxhlet, pH 9.0 and pH 3.9 methods. Percentage weight changes are shown in Table 12. The positive numbers represent a weight gain indicative of a hydration process. From SEM analysis it was

TABLE 7. Oxide Composition of Supercalcine SPC-4

<u>Oxide</u>	<u>Composition, Wt% Oxide</u>
<u>Waste Stream Constituents</u>	
BaO	2.5
CdO	0.2
Cr ₂ O ₃	0.5
Cs ₂ O	4.6
Fe ₂ O ₃	4.8
MoO ₃	8.2
Na ₂ O	0.2
NiO	0.2
P ₂ O ₅	4.3
Rb ₂ O	0.6
RuO ₂	0.5
SrO	1.7
ZrO ₂	7.8
CeO ₂	9.8
La ₂ O ₃	4.9
Nd ₂ O ₃	3.5
Pr ₆ O ₁₁	1.0
Y ₂ O ₃	0.1
Sm ₂ O ₃	0.6
Gd ₂ O ₃	17.0
Ho ₂ O ₃	0.1
<u>Supercalcine Additives</u>	
CaO	2.1
SrO	2.6
Al ₂ O ₃	4.5
SiO ₂	17.6

TABLE 8. Weight Loss of Supercalcine SPC-4 Pellets
After 4 hr in Dry Air^(a)

Element	Weight Loss at 1100°C		Weight Loss at 1500°C		Weight Loss at 1200°C	
	mg ^(b)	% ^(c)	mg ^(b)	% ^(c)	mg ^(b)	% ^(c)
Na	0.18	4.5	0.39	9.8	1.05	26.1
Rb	0.06	0.8	0.1	3.1	0.25	8.6
Mo	17.5	1.1	5.4	3.7	1.8	11.2
Ru	N.D. ^(d)	N.D.	N.D.	N.D.	0.24	2.4
Ag	0.09	2.5	0.12	2.3	0.29	7.8
Cd	0.13	3.3	0.27	6.8	0.70	17.8
Cs	0.94	0.8	4.4	3.4	13.5	11.2

(a) Presintered for 1 hr at 1200°C

(b) All Pellets referred to in this table were 2.8 g with 3.5 cm² of exposed surface area.

(c) Percentage weight losses are based on amount of element originally present.

(d) Element not detected

TABLE 9. Weight Loss of Supercalcine SPC-4 Pellets
After 1 hr Sintering at 1200°C

Element	Absolute Weight loss, ^(a) mg	Relative Weight Loss, ^(b) %
Na	0.52	12.9
Rb	0.91	6.1
Mo	8.23	5.2
Ru	2.53	24.4
Ag	0.16	4.3
Cd	0.39	9.7
Cs	12.29	9.9

(a) Pellets were 2.8 g with 3.5 cm² of exposed surface area.

(b) Percentage weight losses are based on the amount of element originally present.

TABLE 10. Typical Leachability Values of Simulated Waste Glasses(a)

Test	Range ^(a) g/cm ² -d	% wt loss/d
Soxhlet	5.57×10^{-5} to 7.3×10^{-6}	0.19 to 1.45
pH 9.0	1.74×10^{-4} to 4.85×10^{-6}	0.13 to 4.52
pH 3.9	4.53×10^{-3} to 1.46×10^{-6}	0.04 to 100

(a) Surface area assumed 260 cm²/g

determined that the surface structure of the Al₂O₃-coated calcine became indistinct upon leaching. This suggests a loss of Al₂O₃ crystalline structure.

The coatings were applied at different temperatures because of substrate temperature limitations. The calcine was coated at 825°C, and the coating contained kappa and gamma alumina. The supercalcine was coated at a higher temperature of 1025°C and contains only alpha alumina. The coated calcine particles gained more weight upon leaching than the coated supercalcine particles. Thus, leachability of alumina coatings may be dependent upon coating temperature and alumina phase.

Supercalcine cores and pellets were leach tested for 72 hr by the Soxhlet and pH 4 and pH 9 static tests. Four differently prepared samples were tested as described in Table 13. Leach results are reported in Table 14 as total weight loss and in IAEA units of weight loss per cm² per day. The IAEA results are listed both for the typical initial surface area and for the final leached surface area. Further analysis is being conducted on the samples by SEM, and the leach solutions will be analyzed for specific ions.

Additional Soxhlet tests were conducted on various supercalcine SPC-4 forms of the inner core material in the multibarrier concept. Soxhlet leachabilities are compared in Table 15.

IMPACT RESISTANCE

Impact resistance is an important parameter in risk analysis because it indicates the potential for air dispersion. In order to provide some knowledge

TABLE 11. Leaching Resistance of Selected Phases⁽⁹⁾

Phase	Structure Type	Soxhlet Leachability (% wt change) ^(a)			
		1st 24 h.	2nd 24 h.	3rd 24 h.	Overall
Al ₂ O ₃ (Coors A-99)	Corundum	-0.07	-0.00	-0.01	-0.08
Silica glass-SiO ₂	Amorphous	-0.13	-0.02	-0.04	-0.19
Kyanite, Al ₂ O ₃ SiO ₂	Kyanite	-0.41	-0.15	-0.17	-0.72
CeO ₂	Fluorite	+0.23	+1.15	-0.09	+1.29 ^(b)
(Ba,Sr) ZrO ₃	Perovskite	-0.01	-0.27	-0.38	-0.66
Nd ₂ MoO ₆	Scheelite-related	-0.13	-0.10	-0.10	-0.33
Nd ₂ Zr ₂ O ₇	Fluorite	-0.13	-0.17	-0.17	-0.65
Nd ₂ Ti ₂ O ₇	Fluorite-related	-0.2	-0.04	-0.05	-0.29
(Ba,Sr)TiO ₃	Perovskite	-1.5	-0.52	-0.48	-2.5
(Ba,Sr)MoO ₄	Scheelite	-2.7	-2.3	-1.9	-6.8
(Ba,Sr)FeO _{2.8}	Perovskite	-42.0	-8.7	-8.0	-59.7

(a) Surface area was not measured.

(b) Hydration rather than leaching.

TABLE 12. Leach Rates of Al₂O₃-Coated Particles

	Time Period, hr	% Weight Change(a)		
		pH9, 25°C	pH4, 25°C	Soxhlet, 100°C
Supercalcine Core	1st 24	+0.05	0	-0.02
	2nd 24	0	0	0
	3rd 24	+0.01	0	+0.07
	72 total	+0.06	0	+0.05
Calcine Frit Core	1st 24	+0.37	+0.60	+0.50
	2nd 24	+0.13	+0.14	+0.21
	3rd 24	+0.08	+0.25	+0.21
	72 total	+0.48	+0.99	+0.92

(a) Surface area not obtained.

TABLE 13. Description of Supercalcine Leach Samples

<u>Samples</u>	<u>Preparation Technique</u>	<u>Typical BET Surface Area Before Test</u>
C-1 to C-3	Disc-pelletized ~0.44-in.-dia cores fired at 1150°C	1400 cm ² /g
	Disc-pelletized 0.35-in.-dia cores (5% montmorillonite added) fired at 1150°C	340 cm ² /g
SPC-2	Pressed at 20000 psi, sintered at 1125°C - 6 hr, -42+60 mesh	430 cm ² /g
SPC-2P	Pre-fired at 800°C for 1-1/2 hr, pressed at 20000 psi, sintered at 1125°C for 6 hr, -42+60 mesh	380 cm ² /g

TABLE 14. Leach Results for SPC-2 Samples

Sample	Leach ^(a) Test	Leached BET Surface Area, cm ² /g	wt% Loss	IAEA Units ^(b) g/cm ² /day	IAEA Units, ^(c) g/cm ² /day
C-1	Soxhlet	3600	0.64	5.93×10^{-7}	1.52×10^{-6}
C-2	pH 9	2900	0.30	3.45×10^{-7}	7.14×10^{-7}
C-3	pH 4	1600	0.31	6.46×10^{-7}	7.38×10^{-7}
C-4	Soxhlet	150	0.06	1.33×10^{-6}	5.88×10^{-7}
C-5	pH 9	80	0.01	4.17×10^{-7}	9.80×10^{-8}
C-6	pH 4	120	0.09	2.50×10^{-6}	8.82×10^{-7}
SPC-2-24	Soxhlet	3000	1.90	2.11×10^{-6}	1.47×10^{-5}
SPC-2-25	pH 4	720	0.39	1.81×10^{-6}	3.02×10^{-6}
SPC-2-26	pH 9	670	0.06	2.99×10^{-7}	4.65×10^{-7}
SPC-2P-1	Soxhlet	1800	0.93	1.72×10^{-6}	8.16×10^{-6}
SPC-2P-2	pH 4	1200	0.49	1.36×10^{-6}	4.30×10^{-6}
SPC-2P-3	pH 9	600	0.12	6.67×10^{-7}	1.05×10^{-6}

(a) all for 72 hr

(b) based upon leached surface area

(c) based upon typical initial surface area

TABLE 15. Soxhlet Leachabilities for Various Supercalcine
SPC-4 Core Materials

Material	Coating	Weight change in 72 hr, wt%
2-mm Cores	none	-0.34
2-mm Cores	PyC	+0.01 to +0.77
2-mm Cores	PuC/Al ₂ O ₃	+0.04 to +1.70
6-mm Cores	Corning 1723 glass	-0.09
6-mm Cores	Corning 7740 glass	-0.08
6-mm Cores	Ferro D1230 glass	-0.86

of the consequences of impact, canisters containing simulated waste glass have been drop tested.⁽¹⁰⁾ In the present study, a laboratory-scale impact test was used to compare multibarrier waste forms to previously tested reference waste glass specimens.⁽⁶⁾ It is difficult to produce multibarrier samples for impact testing equivalent to those used for the reference glass process. The reference glass samples were produced by diamond core drilling of larger solid specimens. The composite nature of multibarrier waste forms make core drilling difficult because the drilling cuts through the inner cores and their protective coating. Also, since in the multibarrier waste form the radio-nuclides are contained only in the core, impact damage to the core is of major concern, rather than the complete composite.

The approach to determine impact behavior was to first consider the matrix and inner core independently. The entire inner core-matrix composite was then impacted and an attempt was made to separate the inner core for analysis. Because actual inner core materials were limited in quantity, conventional glass beads and aluminum beads were often substituted.

The impact behavior of various waste form component materials was examined by impacting right circular cylindrical specimens (0.50-in. OD x 0.50-in. long and 1.25-in. OD x 1.25-in. long) in the punch and die developed for previous PNL work.⁽⁶⁾ The die was purposely oversized to offer minimal restraint to the sample fracture, and the punch contained swirl chambers to minimize the amount of fine material ejected during impact. The punch was struck by a weight running on linear ball-bearings (160 ft-lb maximum energy). The fine particles produced were sized by sieving for +37- μ m particles. In addition, the surface area of the impacted sample was determined as a function of impact energy. Impact behavior was also determined for uncontained glass marble specimens.

Compressive strength has been determined for supercalcine SPC-2 and calcine/frit coated by CVD with 33-39 μ m of Al_2O_3 , for uncoated cores, and for PyC- and SiC-coated simulated waste. Individual cores were tested on the Instron^(a) machine using a ram speed of 0.002 in./min. For comparison,

(a) Instron Testing Machine, Instron Corporation

cores were assumed to be spherical using the ram gap as the approximate diameter. Results are listed in Table 16.

Strength is increased by at least a factor of two upon coating with Al_2O_3 . The compressive strength of PyC- and SiC-coated waste is greater than Al_2O_3 -coated cores. In comparing strengths, one must note the differences in coating thickness and core diameter.

To obtain perspective on how well a spherical sample can withstand impact forces, impact tests were conducted on marbles of ICM-11 and soda-lime glass and on SPC-2 cores. Particles size distribution was determined by sieve analysis.

Screening analyses were not reproducible because of fines agglomeration. The marbles or cores were impacted one at a time; thus the impact forces were extremely high. Surface area measurements by the BET technique allow penetration of the agglomerates. Surface area of the impacted samples is plotted in Figure 12. Results of impaction studies on 0.44-in.-OD x 0.50-in.-long right circular cylinders of ICM-11 glass are included for comparison. Although the total surface area of SPC-2 is much greater than that of waste glass or soda-lime marbles, the actual increase in surface area with impact is less. The

TABLE 16. Results of Compressive Strength Tests for Various Waste Forms

Core	Coating	Diameter, in.	Compressive Strength, psi
Calcine/Frit	Uncoated	0.0503 ± 0.0060	3050 ± 1121
Calcine/Frit	$33 \mu\text{m Al}_2\text{O}_3$	0.0576 ± 0.0027	6175 ± 1672
Supercalcine	Uncoated	0.0576 ± 0.0032	4409 ± 3877
Supercalcine	$39 \mu\text{m Al}_2\text{O}_3$	0.0625 ± 0.0023	7290 ± 3473
Simulated Waste ^(a)	$30 \mu\text{m PyC}$	0.0170 ± 0.0018	25807 ± 4728
Simulated Waste	$200 \mu\text{m PyC}$		
	$18 \mu\text{m SiC}$	0.0110 ± 0.0020	10599 ± 6196
Simulated Waste	$60 \mu\text{m PyC}$	0.0126 ± 0.0027	21006 ± 10377

(a) Fluid Bed Calcine

FIGURE 12. Surface Area of Supercalcine and Other Waste Forms After Impact Tests at Various Forces

surface area for SPC-2, waste glass, and soda-lime increases upon impact at 158.4 ft-lb by a factor of 4, 556, and 521, respectively. The impact results for soda-lime marbles, ICM-11 marbles, and ICM-11 right-circular cylinders do not significantly differ on a surface area/gm basis.

Since the supercalcine cores contained considerable porosity, additional impact tests were conducted on hot-pressed supercalcine, which represents a product of optimum density. To determine the best possible impact resistance of a ceramic product, tests were also conducted on a sample of Al_2O_3 grinding media.^(a) The results for both samples after impact at 158.4 ft-lb are compared with the previous ICM-11 glass cylinder in Figure 13. The supercalcine, which is denser than glass, produced half as many fines <37 μm as glass. The impact resistance of the Al_2O_3 grinding media indicates that optimum ceramic products might have one fifth as many fines <37 μm as glass.

The next phase of the impact tests was to determine how the matrix material, alone, withstood impact forces. Four materials (vacuum-cast Pb, Al-12Si, gravity-sintered 410 stainless steel, and copper) were evaluated at various

(a) 85 wt% Al_2O_3 ; 11 wt% SiO_2 ; 2 wt% MgO; 0.6 wt% Na_2O

FIGURE 13. Glass and Ceramic Waste Forms After Impact of 158.4 ft-lb

impact forces. The samples were right circular cylinders 0.50-in. OD x 0.50-in. long.

Because of their ductility, the metal samples were merely compacted by the impact force. Only one sample shattered upon impact; this was the gravity-sintered copper sample at 158.4 ft-lb impact. The results of this test are presented as percent compaction versus impact force in Figure 14. The vacuum-cast Al-12Si and gravity-sintered 410 stainless steel matrix offer more resistance to compaction than the vacuum-cast Pb and gravity-sintered copper.

The next series of impact tests to evaluate metal matrices was conducted on right circular cylinders (1.25-in. OD by 1.25-in. long) with the same impact force (158.4 ft-lb.) Five vacuum-cast metals were evaluated: Pb, Pb-6Sn, Pb-10Sn, Al, and Al-12Si. Pure matrix samples were compared to those containing 3-mm and 6-mm commercial glass beads or 10-mm waste glass marbles. Removal of the marbles from the aluminum matrices was impossible, and thus the relative compaction or reduction in height was used as an indication of impact resistance. A histogram is presented in Figure 15 for various matrix materials and marbles composites.

FIGURE 14. Height Compaction of Various Metal Matrices in Impact Tests

FIGURE 15. Relative Height Compaction of Several Metal Matrices After Impact at 158.4 ft-lb

The resistance to compaction is increased upon alloying for both Pb and Al. The Al-12Si and Al matrices offer better compaction resistance than either Pb or Pb alloys. In general, the compaction is greater when glass marbles (3 to 10 mm in diameter) were added. This is probably due to the reduction of metal volume (35% for optimum packing of marbles).

The last and most difficult series of impact tests was to determine the fragmentation of the inner core contained within a matrix. Several preliminary tests were purely qualitative because the core could not be successfully separated from the matrix. Quantitative results were obtained for glass marbles within a vacuum-cast Pb-10Sn matrix and for CVD Al_2O_3 coated supercalcine in a 410 stainless steel matrix. These tests were successful because the glass marbles and fragments could be removed from the impacted matrix by manually cutting away the matrix and the impacted 410 stainless steel matrix was removed by magnetic separation.

The glass marble Pb-10Sn matrix samples consisted of 1.25-in. OD x 1.25-in.-long right circular cylinders and were impacted at 158.4 ft-lb. A photograph of the impacted samples is shown on Figure 16. The impact resulted in 20% compaction of the samples. The Pb-10Sn matrix was removed with metal cutters. Many of the marbles were not fractured. All the marbles and fragments were carefully collected during metal removal. The glass loading in the matrix was ~60 vol%. The wt% of unfractured marbles for 10-mm waste glass, marbles and 6-mm and 3-mm chemical glass marbles was 13.17%, 31.01%, and 76.35%, respectively. The majority of the fractured glass had a particle size greater than 500 μm for all three samples. The fines distribution of the fractured glass below 500- μm is illustrated in Figure 17. For the worst case, the wt% of fines less than 37 μm does not exceed 0.15%.

The 410 stainless steel, gravity-sintered samples contained 2-mm supercalcine cores CVD coated with 4 μm of PyC and 39 μm of Al_2O_3 . One sample, containing only 40% loading of cores instead of the normal 60%, contained cores coated with only 39 μm of Al_2O_3 . The impact samples were 0.52 in. dia. by 0.50-in. long.

Supercalcine was separated from the 410 stainless steel by use of an electromagnet. Particle size distribution for the supercalcine and metal

FIGURE 16. Impacted Pb-10Sn Matrices with Glass Marbles of Varying Diameters

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

matrix is plotted on Figure 18 for various impact forces. The wt% of fines finer than $37\text{ }\mu\text{m}$ does not exceed 2%. The effect of supercalcine loading is shown in Figure 19. Two samples, one at 40 wt% and the other at 60 wt% loading were impacted at 158.4 ft-lb. The 40% loading had greatly lowered fine particulate formation. The fines distribution for supercalcine is compared to that for an ICM-11 sample in Figure 20. The waste loading should be taken into account to provide a meaningful comparison. The fine particulate from the supercalcine would contain 2.4 times the waste content of a typical waste glass.

To obtain a better understanding of the method of impact failure in the gravity-sintered composite, the 40% and 60% loading samples were impacted with restricted ram travel. Upon contact, the ram was restricted to 0.020 in. of travel or impact. Thus, the samples were not completely crushed and micrographs could be taken after impact as shown in Figure 21. Vertical impact for this sample was restricted to 0.020 in.

For both cases the cores were cracked although the metal matrix was not damaged. The gravity-sintered matrix appears not to have provided significant impact resistance to the composite. As shown in Figure 14, the gravity

FIGURE 18. Particle Size Distribution for Impacted Al_2O_3 -Coated Supercalcine in a 410 Stainless Steel Matrix

FIGURE 19. Effect of Supercalcine Waste Loading upon Particle Size Distribution After Impact at 158.4 ft-lb

FIGURE 20. Particle Size Distribution of Impacted ICM-11 and Supercalcine Samples

FIGURE 21. Supercalcine SPC-1 Cores Coated with $39\ \mu\text{m}\ \text{Al}_2\text{O}_3$ in a Gravity-Sintered 410 Stainless Steel Matrix

sintered matrix, by itself, has considerable impact resistance. It is apparent that the dilution of the matrix by the addition of supercalcine cores greatly decreases the impact resistance of the metal matrix.

One of the major problems in comparing impact results of the composite waste forms to the glass monolith is the variation in sample configuration. Sample size varied because of material limitations, inner core diameter, and in some cases, convenience of preparation. For example, glass marble waste forms were 1.25 in. in diameter since the marble diameter was greater than the standard 0.50-in.-dia sample size; CVD-coated supercalcine was restricted to a diameter of 0.50 in. because of the limited supply of coated cores. To allow at least an approximate comparison between the impacted samples, an additional 158.4 ft-lb impact test was conducted on two ICM-11 waste glass samples of 0.44-in. and 1.25-in. diameters. The results are plotted in Figure 22. It is interesting to note that although the sample volume was increased by a factor of 20, the percent fines less than 37 μm were reduced only by a factor of 9.

FIGURE 22. Effect of ICM-11 Glass Sample Size Upon Particle Size Distribution After Impact at 158.4 ft-lb

EFFECTS OF RADIATION ON SUPERCALCINE

Supercalcine composition SPC-2 was doped with Cm_2O_3 to the 3 wt% level. X-ray diffraction, stored energy, and density measurements were made initially and at approximately three month intervals to assess the effects of the dopant. Dose levels in excess of 10^{18} α/g have been reached. For reference, a dose of 1.2×10^{18} α/g is equivalent to 200 years storage for supercalcine with 80% waste loading.

The initial effects of the curium dopant on phase behavior are illustrated in Table 17 and indicate phases that the dopant may have affected. From Table 17 it would appear by comparison of the diffraction angles measured with no dopant and at α dose = 0 (with dopant) that the curium may have gone into both the apatite phase and the tetragonal phase. Both of these phases shifted in diffraction angle by over $0.1^\circ 2\theta$ while the fluorite phase shifted only 0.05° . An additional manifestation noted after doping with curium was that of overall peak broadening. As illustrated in Table 18 all three of the major phases exhibited some broadening, but again, those that shifted diffraction angle seemed to broaden the most.

TABLE 17. Peak Positions for the Major Phases Noted in SPC-2 Supercalcine Before and After Doping

Major Phases (diffraction peak)	Diffraction Angle	
	No Dopant	With Dopant
Fluorite (220)	$48.050^\circ 2\theta$	$48.000^\circ 2\theta$
Tetragonal (111)	29.985	29.870
Apatite (213)	48.650	48.515

TABLE 18. Peak Broadening in SPC-2 Supercalcine

Major Phases (diffraction peak)	Peak Width at Half Maximum		
	No Dopant	With Dopant	% Change
Fluorite (220)	$0.340^\circ 2\theta$	$0.395^\circ 2\theta$	16
Tetragonal (111)	0.265	0.365	38
Apatite (213)	0.280	0.410	46

As α -dose increases, the apatite phase is seen to continue shifting toward lower angles and by a dose of 5.0×10^{17} has shifted approximately $0.1^\circ 2\theta$ from the original value. Both the fluorite phase and the tetragonal phase appear to remain at their initial 2θ values up to a dose of 5.0×10^{17} α/g .

Since the fluorite phase has changed very little with radiation damage and also since initial measurements indicated essentially no change after doping, the (220) fluorite peak was used as an internal standard. Computing the ratios of integrated intensities (i.e., apatite/fluorite; tetragonal/fluorite), the results appear as in Figure 23. There is a decrease in the intensity of the apatite peak while the tetragonal phase shows a slight increasing tendency. After a dose of 1.5×10^{18} α/g the apatite peak (213) has completely disappeared. Other apatite peaks are still barely detectable. It is estimated that by a dose of 2×10^{18} α/g no apatite peaks will remain. The results indicate that in supercalcine SPC-2 the apatite phase will become amorphous with radiation damage while the fluorite and tetragonal phases will remain relatively unaffected.

FIGURE 23. Ratios of Integrated Intensities (apatite/fluorite and tetragonal fluorite)

Figure 24 illustrates the variation in lattice constants for the fluorite phase calculated based on the as-measured position of the (220) peak. The variation from the mean value, $a_0 = 5.3637 \text{ \AA}$ was 0.1%, indicating very good correlation from run to run. Using the slight variations in measurements of the fluorite (220) peak to correct the measurements of apatite peak positions, the (213) and the (211) apatite peaks were used to calculate lattice constant values in the hexagonal unit cell. Figure 25 illustrates a_0 and c_0 values for apatite in supercalcine as a function of radiation dose. It can be seen from this figure that the apatite unit cell is expanding in the basal plane (a direction) as a_0 goes from $9.5856 \text{ \AA}$ initially to $9.7049 \text{ \AA}$ after $1.5 \times 10^{18} \text{ \alpha/g}$. Along with this expansion is a corresponding contraction in the c direction from $7.0299 \text{ \AA}$ at to $7.0081 \text{ \AA}$.

Even though the tetragonal phase shows a slight increasing tendency in integrated intensity measurements via the main diffraction peak, it was not possible to calculate lattice constants for the tetragonal cell because of extremely weak secondary peaks or overlap with other diffraction peaks.

Stored energy and density measurements were determined in addition to the X-ray diffraction data as shown in Figures 26 and 27. The energy release reaches a maximum of about 10 cal/g near $5 \times 10^{17} \text{ \alpha/g}$ dose and then decreases. Also the release curve (not shown) indicates that complete annealing is not

FIGURE 24. Variation of the Lattice Constant a_0 for the Fluorite Phase in Supercalcine SPC-2 as a Function of Alpha Dose

FIGURE 25. Variation of the Lattice Constants a_0 and c_0 for the Apatite Phase in Supercalcine SPC-2 as a Function of Alpha Dose

attained at 600°C (the upper limit of the calorimeter) and that a substantial energy release may occur at temperatures above 600°C.

The measured density decreased from 4.18 to 4.12 at a dose of 1.7×10^{18} α/g . This corresponds to a density decrease or volume expansion of 1.4%. The theoretical concentration of apatite is 12.5%. Thus the total volume expansion due to apatite would be 0.18%. The results of the apatite X-ray diffraction data can be used to estimate a volume expansion by considering the expansion and contraction of the unit cell lattice constants, a_0 and c_0 , respectively. A volume expansion of 3.6% is estimated from X-ray diffraction data, which suggests that other phases besides apatite may be contributing to the volume expansion.

FIGURE 26. Effect of Alpha Dose on the Stored Energy of Curium-Doped Supercalcine

FIGURE 27. Effect of Alpha Dose on the Density of Curium-Doped Supercalcine

CONCLUSIONS AND RECOMMENDATIONS

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

- Simulated waste-glass marbles encapsulated in a vacuum-cast Pb-10Sn matrix
- Uncoated sintered supercalcine pellets encapsulated in a vacuum-cast Al-12Si matrix
- Glass-coated sintered supercalcine pellets encapsulated in a vacuum-cast Al-12Si matrix
- PyC/Al₂O₃ CVD-coated supercalcine encapsulated in a gravity-sintered Cu matrix.

Development of these multibarrier waste forms is discussed in Multibarrier Waste Forms Part I: Development.⁽¹⁾

The characterization of the four waste forms can be summarized by comparison of volatility, impact resistance, and leach resistance data. This is presented in Figures 28 and 29, Table 19, and Table 20, respectively. The data is somewhat limited as the following were not studied:

- leach resistance of the metal matrices
- impact resistance of uncoated and glass-coated supercalcine cores
- volatility resistance of glass coatings
- long-term reaction between the metal matrix and the inner waste core.

Although studies are being continued in these areas, some important conclusions can still be drawn from the available data.

The total volatility of supercalcine is less than that of 72-68 waste glass, as shown in Figure 28. Depending on which supercalcine formulation (SPC-2 or SPC-4) and temperature is selected, the volatility of supercalcine is between 3 and 30 times less than that of glass. The volatility of Cs in supercalcine is an order of magnitude less than the volatility of Cs in 72-68 waste glass as shown in Figure 29. Cesium is the major volatile component.

FIGURE 28. Total Volatility of Glass and Supercalcine Waste Forms

The cesium volatility of supercalcine is dependent upon formulation as indicated by the differing slopes for SPC-2 and SPC-4. Supercalcine SPC-4 has much lower volatility than SPC-2 at low temperatures, whereas above 1100°C SPC-2 has the lower volatility. This illustrates a possible effect of waste stream variations on supercalcine volatility.

It is difficult to compare the impact resistance of composite waste forms: sample sizes vary and separation of matrix and inner core materials can be difficult. The results in Table 19 illustrate the fraction of waste released per

FIGURE 29. Cesium Volatility of Glass and Supercalcine Waste Forms

unit volume of waste form. Although the release rate for glass marbles in a metal matrix is 13 times less than that for monolithic glass, the multibarrier waste form would require 1.7 times more canisters to contain an equivalent amount of waste. Thus, the impact resistance of the multibarrier form may be only 8 times greater than the impact resistance of the glass monolith from a "total risk" standpoint.

Some general conclusions in comparison to glass monoliths can be made from Table 19:

TABLE 19. Calculated Nuclear Waste Release After Impact at 158.4 ft-lb

Material	Sample Size, in.		Coating	Matrix	Waste Content, vol%	Particle Size After Impact, wt% <37 μ m	Waste Release, g/cm ³ x 10 ⁻⁴
	Diameter	Length					
Supercalcine Hot Pressed	0.44	0.50	none	none	75	4.4	1600
Supercalcine ^(a) Cores	0.50	0.50	PyC/Al ₂ O ₃	410SS	34	2.0	200
Supercalcine ^(b) Cores	0.50	0.50	PyC/Al ₂ O ₃	410SS	23	0.4	28
ICM-11 Glass	0.44	0.50	none	none	35	9.0	1100
ICM-11 Glass	1.25	1.25	none	none	35	1.0	120
ICM-11 Glass ^(a) Marble	1.25	1.25	none	Pb-10Sn	21	0.1	9

(a) 60-vol% packing

(b) 40-vol% packing

- Glass marbles in a metal matrix offers approximately an order of magnitude increase in impact resistance.
- CVD PyC/ Al_2O_3 -coated supercalcine in a gravity-sintered 410 SS matrix improves the impact resistance by 1 to 2 orders of magnitude, depending upon vol% loading.
- Hot-pressed supercalcine may offer no increase in impact resistance.

Leaching tests of greater complexity than Soxhlet weight loss need to be run on the multibarrier products to provide detailed leach resistance analyses. From the data in Table 20 and earlier in the text, one can conclude that supercalcine may not offer a significant increase in leach resistance over waste glasses. Coatings appear to offer improved leach resistance, especially in the case of PyC and Al_2O_3 applied by chemical vapor deposition. Coatings would provide a barrier for a finite period of time, during which the hazard index of the inner core would be decreasing. For example, a 1-mm glass coating with a leach resistance of 10^{-6} g/cm²-d would provide a barrier for over 600 years. Recent studies at PNL on graphite powder in distilled water at 95°C have suggested that the leach resistance of PyC is $\sim 1 \times 10^{-9}$ g/cm²-d.⁽¹⁰⁾ Thus a 50- μm coating of PyC could provide thousands of years of protection.

A fourth area that needs to be considered in the characterization of waste forms is the effect of radiation on the primary stability parameters. For example, the radiation environment may create chemical or physical changes to the waste form which will cause a decrease in the leach, volatility, or impact resistance. The present studies of supercalcine have only determined what chemical or physical changes can be expected as summarized in Table 20. Further studies at PNL are being conducted on the leach, volatility, and impact resistance of radiation-damaged supercalcine. As is illustrated in Table 21, supercalcine behaves similarly to glass under alpha particle exposure. One major exception is that stored energy is less, which may be due to the limited temperature range of 600°C of the apparatus (stored energy release in ceramics may occur above this temperature). The other difference is that crystalline products may exhibit phase changes. After an equivalent of 200 years of alpha particle exposure, supercalcine showed no apatite phase, which suggested the formation of an amorphous phase.

TABLE 20. Comparison of Soxhlet Leach Rates of Multibarrier Materials

Material	% Weight Change Over 72 hr
Waste Glass	-0.30 to -1.45 ^(a)
Supercalcine Cores	-0.3 to -1.90
PyC CVD Coating	+0.01 to +0.77
Al ₂ O ₃ CVD Coating	+0.04 to +1.70
Glass Coating	-0.08 to -0.86

(a) 24-hr period for the high value

TABLE 21. Effect of Exposure to ²⁴⁴Cm on Supercalcine and Waste Glasses

Waste Forms	Stored ^(b) Energy, cal/g	Density Change, %	Phase Stability
Glass	20-50	+ 1%	No observed degradation
Supercalcine	10	-1.5%	Some degradation ^(a) of phases

(a) Apatite disappeared after 200-yr equivalent exposure.

(b) At ≤600°C

The following recommendations are suggested based on the contents of this report:

- Select glass marbles encapsulated in a cast lead alloy as the multibarrier concept for further development.
- Select uncoated sintered supercalcine pellets encapsulated in a cast aluminum alloy for further development if a crystalline multibarrier product is desired.
- Develop improved bonding in gravity-sintered matrices.
- Investigate less complex methods to apply barrier coatings.
- Determine leach resistance of metal matrix waste forms.
- Quantify effect of radiation damage on supercalcine integrity.
- Make comparative impact testing of metal matrix composites.
- Investigate long-term metal matrix-inner waste core reactions.

All of the above recommendations are presently within PNL program plans except for improved gravity-sintered matrices and less complex barrier coatings. Studies are being initiated to lower the coating temperature for PyC to enable coating of glass, as well as ceramic waste forms. Scaled-up demonstrations of uncoated glass marbles and supercalcine pellets encapsulated in metal alloys are underway.

ACKNOWLEDGEMENTS

The authors are indebted to T. D. Chikalla and R. P. Turcotte for their help and suggestions. In addition to the authors, major contributors to this program were F. P. Roberts, W. J. Gray, L. R. Bunnell, R. A. Wheeler, and J. E. Gose.

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