A Review of High-Level Waste Form Properties

J. M. Rusin

December 1980

**Prepared for the U.S. Department of Energy
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**Pacific Northwest Laboratory
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Richland, Washington 99352

SUMMARY

This report is a review of waste form options for the immobilization of high-level-liquid wastes from the nuclear fuel cycle. This review covers the status of international research and development on waste forms as of May 1979. Although the emphasis in this report is on waste form properties, process parameters are discussed where they may affect final waste form properties.

A summary table is provided listing properties of various nuclear waste form options. It is concluded that proposed waste forms have properties falling within a relatively narrow range. In regard to crystalline versus glass waste forms, the conclusion is that either glass ^{or} ~~or~~ crystalline materials can be shown to have some advantage when a single property is considered; however, at this date no single waste form offers optimum properties over the entire range of characteristics investigated. A long-term effort has been applied to the development of glass and calcine waste forms. Several additional waste forms have enough promise to warrant continued research and development to bring their state of development up to that of glass and calcine. Synthetic minerals, the multibarrier approach with coated particles in a metal matrix, and high pressure-high temperature ceramics offer potential advantages and need further study.

Although this report discusses waste form properties, the total waste management system should be considered in the final selection of a waste form option. Canister design, canister materials, overpacks, engineered barriers, and repository characteristics, as well as the waste form, affect the overall performance of a waste management system. These parameters were not considered in this comparison.

CONTENTS

SUMMARY	iii
ACRONYMS AND ABBREVIATIONS	xiii
INTRODUCTION	1
RADIOACTIVE WASTES	1
WASTE FORM OPTIONS	9
REVIEW OF WASTE FORM DEVELOPMENT IN THE UNITED STATES	13
GLASS	13
SINTERED CERAMIC	23
GLASS CERAMIC	27
HOT PRESSED CERAMICS	28
COATINGS	33
CONCRETE	36
METAL MATRIX	40
REVIEW OF INTERNATIONAL WASTE FORM DEVELOPMENT	47
GLASS	47
Canada (AECL)	47
England (AERE)	51
France (Marcoule)	56
SINTERED CERAMIC	57
Japan (PNC)	57
GLASS CERAMIC	61
Germany (HMI)	61
Japan (PNC)	64

HOT PRESSED CERAMICS	.	.	.	.	.	.	.	.	.	.	66
Australia (ANU)	.	.	.	.	.	.	.	.	.	.	66
Sweden (ASEA)	.	.	.	.	.	.	.	.	.	.	72
COATINGS	.	.	.	.	.	.	.	.	.	.	75
Austria (SGAE)	.	.	.	.	.	.	.	.	.	.	75
CONCRETE	.	.	.	.	.	.	.	.	.	.	75
Belgium (Eurochemic)	.	.	.	.	.	.	.	.	.	.	75
METAL MATRIX	.	.	.	.	.	.	.	.	.	.	76
Austria (SGAE)	.	.	.	.	.	.	.	.	.	.	76
Belgium (Eurochemic)	.	.	.	.	.	.	.	.	.	.	77
COMPARISON OF WASTE FORM PROPERTIES	.	.	.	.	.	.	.	.	.	.	81
CHEMICAL DURABILITY	.	.	.	.	.	.	.	.	.	.	81
VOLATILITY	.	.	.	.	.	.	.	.	.	.	83
IMPACT	.	.	.	.	.	.	.	.	.	.	87
RADIATION STABILITY	.	.	.	.	.	.	.	.	.	.	91
BULK PROPERTIES	.	.	.	.	.	.	.	.	.	.	93
CONCLUSIONS	.	.	.	.	.	.	.	.	.	.	97
ACKNOWLEDGMENT	.	.	.	.	.	.	.	.	.	.	101
REFERENCES	.	.	.	.	.	.	.	.	.	.	103

FIGURES

1	Alternative Waste Form Options	10
2	Leach Rate as a Function of Time for Cs, Sb, Sr, Pu, and Cm in 72-68 Glass	16
3	Splitting Tensile Strength of Hot-Pressed Cement Containing PW-4c	32
4	Leach Rates of Cs-137 from Grouts with Various Mix Additives . .	39
5	Laboratory Scale Operations Used to Produce Cement Storage Forms from High-Level Wastes	42
6	Canadian Waste Glass Leaching Experiment	49
7	Ceramic Encapsulation of Nuclear Waste Using ASEA's High-Pressure Technology	74
8	Embedding of Glass Beads into a Lead Matrix	78
9	Gross Weight Loss of Waste Forms After 4 hr in Dry Air	88
10	Cesium Loss from Waste Materials in Four Hours at Various Temperatures	89
11	Surface Area of Supercalcine and Other Waste Forms After Impact Tests at Various Forces	90
12	Particle Size Distribution of Waste Forms After Impact of 158.4 ft-lbs	90
13	Positive Dilatation Due to Internal Alpha Radiolysis of Borosilicate Glasses Containing ^{244}Cm or ^{238}Pu	92
14	Effect of Radiation on the Density of (A) Waste Solids and (B) Crystalline Phases	94
15	Ratios of Integrated Intensities	95
16	Protective Barriers for HLW During Geologic Disposal	98

TABLES

1	High-Level Waste Forms	2
2	Characteristic Transuranic Radioactive Wastes Stored at Idaho National Engineering Laboratory	3
3	Characteristic Radioactive Wastes from a Nuclear Power Reactor	4
4	Composition of NFS Thorium-Bearing Waste, Tank 8D4	5
5	Estimated Composition of Contents of NFS Waste Tank 8D2	6
6	Allied General Nuclear Services High-Level and Intermediate- Level Waste Compositions	7
7	High-Level Waste Stored in the United States	8
8	Major U.S. Waste Form Development Activities	13
9	Typical Waste Glass Composition	14
10	Reference PNL Waste Glass Compositions	15
11	Vitrification of Hanford Sludges	19
12	Vitrification of Hanford Residual Liquid	20
13	Composition of SRL Glass-Forming Frit	22
14	Comparison of Leachabilities of Heated and Unheated Waste Glasses	23
15	Primary Containment Phases in Current Supercalcine-Ceramics	25
16	Primary Containment Phases Identified in SLA Titanate-Ceramics	27
17	Density of Hot Pressed Ceramics	29
18	FUETAP Mix Composition	30
19	Effect of Mix Composition on FUETAP Concrete	31
20	Coatings Applied in a Fluidized Bed to Particles in the 200- μ m Range	35
21	Multibarrier Waste Form Development One Liter Demonstration	40

22	Seven-Day Leach Rates in 25°C Distilled Stagnant Water for PW-7a Beads in Various Configurations in Lead Matrices	43
23	Results of 10-Day Autoclave Corrosion Test for Lead and Aluminum Alloy	43
24	Corrosion Rates of Candidate Alloys in Deoxygenated Solutions	44
25	Corrosion Rates of Candidate Alloys in Oxygenated Solutions	45
26	International Waste Form Development	48
27	Current Specifications for Canadian Reference Immobilized Waste Package	50
28	Simulated High-Level Canadian Waste Glass Compositions and Range of Leach Rates Observed During 60-Day Test at 100°C	52
29	Comparison of FINGAL and Magnox Waste Compositions	54
30	Composition of AERE Glasses	54
31	Fixation Media for Nuclear Wastes	55
32	Example of Marcoule Glass Compositions	58
33	Leach Rate Values of Marcoule Glasses	58
34	Compositions of Candidate PNC Nepheline Type Sintered Ceramics	59
35	Compositions of Parent Glasses and Crystal Phases of HMI Glass Ceramics	62
36	Conditions for Preparation of HMI Glass Ceramics	63
37	Properties of European Glass and Glass Ceramics Products	65
38	Properties of Glass and Glass Ceramics	65
39	Compositions and Crystal Phases of PNC Glass Ceramics	66
40	Leach Rate of PNC Glass Ceramics	67
41	Effect of Heat Treatment on Crystal Phases and Leach Rate of PNC Glass Ceramics	67
42	Bending Strength, Thermal Expansion and Thermal Shock Resistance of PNC Glass Ceramics	68

43	Properties of D-62 Glass Ceramic Crystallized in Canister During Cooling	68
44	Composition of SYNROC A and SYNROC B	70
45	Summary of Distribution of Radwaste Elements Among SYNROC B Phases	70
46	Corrosion Rate of Lead Alloys in Dry ASSE Salt and Aqueous Solutions Saturated with the ASSE Salt	80
47	Properties of Alternative Waste Forms	82
48	A Leach Rate Comparison of Materials	83
49	Concentration of Fission Products Leached from Glass and Supercalcine Materials	84
50	Matrix Alteration and Cs Solubility After Leaching Copper Borosilicate Glass, Supercalcine, and Titanate Ceramic	85
51	"Reactivity" of Waste Forms in Various Environments	86

ACRONYMS AND ABBREVIATIONS

AA	- Atomic Absorption
AECL	- Atomic Energy of Canada, Ltd.
AERE	- Atomic Energy Research Establishment
AGNS	- Allied General Nuclear Services
ANL	- Argonne National Laboratory
ANU	- Australian National University
ASEA	- Swedish Power and Equipment Corporation
ASSE	- Asse Saltmine, Germany
ASTM	- American Society for Testing Materials
BNL	- Brookhaven National Laboratories
BWR	- Boiling Water Reactor
CRNL	- Chalk River Nuclear Laboratories
CVD	- Chemical Vapor Deposition
CWS	- Chemical Warfare Service
DIN	- German ASTM
DOE	- U.S. Department of Energy
FB	- Fluidized Bed
FBR	- Fast Breeder Reactor
FINGAL	- British Waste Solidified Process
FP	- Fission Products
FUETAP	- Formed Under Extreme Temperature and Pressure
HAC	- High Alumina Cement
HAW	- High Activity Waste
HIP	- Hot Isostatic Pressing
HLLW	- High Level Liquid Waste
HLW	- High Level Waste
HMI	- Hahn-Meitner Institute
IAEA	- International Atomic Energy Agency
ICM	- In-Can Melting
ICPP	- Idaho Chemical Processing Plant
INEL	- Idaho National Engineering Laboratory
LASL	- Los Alamos Scientific Laboratory

LMFBR - Liquid Metal Fast Breeder Reactor
LOTES - Eurochemic Waste Solidification Process
LWR - Light Water Reactor
MINERVA - Eurochemic Waste Solidification Process
MTU - Metric Ton Uranium
MWD - Megawatt Day
NCS - Noncrystalline Solid
NFS - Nuclear Fuel Services
ORNL - Oak Ridge National Laboratory
PAMELA - German (Gelsenberg A.G.) Waste Solidification Process
PITC - Polymer Impregnated Tritiated Concrete
PNC - Power Reactor and Nuclear Fuel Development Corporation
PNL - Pacific Northwest Laboratory
PSU - The Pennsylvania State University
PWR - Pressurized Water Reactor
PYC - Pyrolytic Carbon
SGAE - Austrian Research Center for Atomic Energy
SLA - Sandia Laboratories Albuquerque
SPC - Supercalcine
SRL - Savannah River Laboratory
SRP - Savannah River Plant
SYNROC - Synthetic Mineral (Rock)
TRU - Transuranic
WIPPP - Waste Isolation Pilot Plant Project

INTRODUCTION

During the past 20 years, numerous waste forms and processes have been proposed for solidification of nuclear wastes. The scale of development has ranged from nonradioactive laboratory experiments to full-scale radioactive demonstrations. The primary purpose of this report is to review and summarize current high level waste forms being developed in the United States and in foreign countries. The contents of this report will be useful to direct future waste form research and development, and to assist in high-level waste immobilization decision making.

Waste form development is reviewed with specific attention to waste form properties. Where appropriate, process details are described which may have an affect on final waste form product integrity. For background information, the various types of radioactive wastes and waste form options are described in this introductory section. The next section of the report describes waste forms under development in the U.S. For reference purposes, selected waste forms developed in previous years are mentioned. The contents have been divided into seven basic categories into which all waste forms can be placed as illustrated in Table 1. The second major portion of the report deals with waste forms developed internationally. Waste form properties are summarized in the final section. Comments are provided on comparison of waste form inertness and current development.

RADIOACTIVE WASTES

Radioactive wastes are materials that are contaminated with radionuclides and generally have no designated product or resource value. These wastes are generated from most activities involving radionuclides. Typical sources of radioactive wastes in commercial industry include the power reactor fuel cycle, medical uses, research/development, and irradiation sources. The United States' government generates a substantial quantity of radioactive wastes from its defense, research/development, and other miscellaneous programs. The radioactive wastes generated from these programs consist of virtually everything the radionuclides have contacted. Examples of defense wastes such

TABLE 1. High-Level Waste Forms(a)

Category	Examples
Glass	Borosilicate Phosphate Basalt Aluminosilicate High silica Porous silica
Sintered Ceramic	Sintered supercalcine Sintered calcine Ceramic sponge Sintered titanate
Glass Ceramics	Celsian glass ceramic Recrystallized fusion melts Basalt glass ceramic SYNROC A
Hot Pressed Ceramics	Hot pressed calcine Hot pressed supercalcine Hot isostatic pressed calcine Hot isostatic pressed supercalcine Hot pressed concrete Hot pressed SYNROC B
Coatings	Pyrolytic carbon Al_2O_3 SiC Nickel Glass
Concrete	Cement and liquid waste Cement and calcine Cement and supercalcine Cement and sludge
Metal Matrix	Glass marbles in metal matrix Sintered ceramic cores in metal matrix Cermets Coated glass marbles in metal matrix Coated ceramic cores in metal matrix

(a) Forms for low-activity waste (e.g., asphalt and urea formaldehyde) are not discussed in this report.

as those transuranic wastes stored at Idaho National Engineering Laboratory are described in Table 2. For radioactive wastes generated from commercial operations, government regulations require that they be disposed of in an approved manner in a state or NRC licensed burial ground. Examples of radioactive wastes generated from nuclear power reactors are indicated in Table 3.

There are no commercial fuels reprocessing plants in operation at this time. The Nuclear Fuel Services Facility at the Western New York Nuclear Services Center is the only commercial fuel reprocessing plant to have operated in the United States. The wastes from fuels reprocessing operations are the high-level liquid wastes which contain essentially all fission products and actinide elements except the recovered uranium and plutonium. Other unique wastes include highly radioactive fuel cladding hulls, fission gases released from the fuel pins, and large pieces of equipment. The composition⁽³⁾ of the high-level liquid waste stored at the Western New York Nuclear Service Center is indicated in Tables 4 and 5.

TABLE 2. Characteristic Transuranic Radioactive Wastes Stored at Idaho National Engineering Laboratory⁽²⁾

Rank	Waste Form	% of Total Volume	Plutonium Content		Density lb/ft ³	Fraction of Volume in Drums
			g/ft ³	g/lb		
1	Metal scrap	36	0.090	3.4×10^{-3}	26	0.04
2	Paper and Rags - dry	9	0.037	1.7×10^{-3}	22	0.50
3	Paper and rags - wet	7	0.041	1.5×10^{-3}	27	0.98
4	Filters - CWS	7	0.105	6.3×10^{-3}	17	0.01
5	Second stage sludge	6	0.031	0.4×10^{-3}	71	1.00
6	LSA metal, glass, etc.	5	0.0018	0.1×10^{-3}	24	0.02
7	First stage sludge	5	0.69	10.3×10^{-3}	67	1.00
8	Organic setups	3	0.067	1.0×10^{-3}	65	1.00
9	Unknown	3	0.15	8.3×10^{-3}	19	1.00
10	Concrete, asphalt, etc.	2	0.021	0.3×10^{-3}	48	0.33
Average for all waste forms			0.19	5.4×10^{-3}	34	

TABLE 3. Characteristic Radioactive Wastes from a Nuclear Power Reactor⁽¹⁾

Source	Components, wt%	Density, kg/m ³	Volume m ³ /GWe-yr
HEPA filters	Glass 40	1.6 x 10 ²	5
	Wood 60		
Combustible trash	Paper 23	1.2 x 10 ²	2 x 10 ²
	Plastic 67		
	Rubber 6		
	Wood 3		
	Cloth 1		
Noncombustible trash	Metal 90	2.5 x 10 ²	4.0 x 10 ¹
	Glass 10		
Reactor scrap/failed equipment	Ferrous alloys 100	5 x 10 ²	6
Bead resins	Polystyrene 50	7.2 x 10 ²	2.9 x 10 ¹
	H ₂ O 50		
Powdered resins	Polystyrene 50	6.7 x 10 ²	2.9 x 10 ¹
	H ₂ O		
Filter precoat sludge	Filter aids 40	4.3 x 10 ²	3.4 x 10 ¹
	H ₂ O 60		
Cartridge filters	Filter media 80	5 x 10 ²	5
	H ₂ O 20		
Sulfate concentrate	Na ₂ SO ₄ 25	1.21 x 10 ³	2.6 x 10 ²
	H ₂ O 75		
Borate concentrate	Na ₂ B ₄ O ₇ 10	1.04 x 10 ³	4
	H ₂ O 90		

Spent Fuel from the Nuclear Power Plant, Once-Through Fuel Cycle

Source	Components, wt%	Weight, MTHM/GWe-yr (a)
PWR	Core 79.5	35
	Zircaloy 16.5	
	Hardware 4.0	
BWR	Core 75.4	42
	Zircaloy 21.0	
	Hardware 3.6	
Average LWR	Core 78.0	38
	Zircaloy 18.0	
	Hardware 4.0	

(a) GWe-yr of energy produced by a 2:1 ratio of PWRs and BWRs based on average exposure.

TABLE 4. Composition of NFS Thorium-Bearing Waste, Tank 8D4(a)(3)

Component	Calculated as	Molarity	Quantity, kg	Radioactivity, Ci
Thorium	Th(NO ₃) ₄	1.46	31,955	3.55
Aluminum	Al(NO ₃) ₃	0.35	3,399	--
Fluorine	NaF	0.10	191	--
Nitric acid	HNO ₃	1.03	2,959	--
Phosphorous	HPO ₄ ⁼	0.04	195	--
Boron	H ₃ BO ₃	0.15 ^(b)	423	--
Chromium, nickel, iron	Fe, Cr, Ni nitrates	--See footnote c--		--
Total fission products	M(NO ₃) _x	(~227 kg)	520	2.43 x 10 ⁶
Cesium	CsNO ₃	(19.3 kg)	28.2	7.47 x 10 ⁵
Strontium	Sr(NO ₃) ₂	(6.2 kg)	14.8	4.83 x 10 ⁵
Uranium (loss)	UO ₂ (NO ₃) ₂	(10 kg)	17	--
Volume, liters			45,598	
Temperature, °C			40 - 50	
Specific gravity			1.8	
Solids content, g/L (estimated)			875 - 1052 ^(d)	

- (a) Based on data in NFS revised Safety Analysis Report and data recorded during surveillance of the thorium fuel processing campaign.
- (b) Estimated from data in NFS original Safety Analysis Report.
- (c) Observations recorded during the surveillance of the thorium fuel processing campaign indicate that substantial quantities of stainless steel hull material dissolved in the fuel dissolution operation because of the presence of variable concentrations of fluorides during processing; these same conditions resulted in enhanced corrosion rates on the dissolver vessel. Thus chromium, nickel, and iron have been added in an undetermined quantity to the waste stream. It is not possible to determine precisely how much stainless steel dissolved, as much as 2696 kg of expected hull material was not recovered. It was also reported that the corrosion coupon in the dissolver showed an 8% loss following the first dissolutions in the campaign. The quantity of corrosion products present in tank 8D4 cannot be determined from presently available data.
- (d) The higher figure includes an estimate for the corrosion products.

TABLE 5. Estimated Composition of Contents of NFS Waste Tank 8D2(a)(3)

Compound	Molecular Weight	In Sludge		In Solution	
		Moles (x10 ³)	Kilograms	Moles (x10 ³)	Kilograms
(Na,K) ₂ SO ₄	142.08	--	--	632.1	89,800
(Na,K) NO ₃ /NO ₂	85.01	--	--	12,287	1,090,423
(Na,K) OH	40.01	--	--	385.9	15,400
(Na,K) Cl	58.46	--	--	8.4	500
Fe(OH) ₃	106.85	463.0	49,500	--	--
FePO ₄	150.82	188.9	28,500	8.3	1,250
Cr(OH) ₃	103.00 ^(b)	37.6	3,811	20.8	2,100
Ni(OH) ₂	92.71 ^(b)	17.6	1,632	8.3	750
Al(OH) ₃	77.98	10.7	830	--	--
AlF ₃	83.98			18.7	1,570
Rare Earth (M(OH) ₃) ^(c)	194.9	8.3	1,620	--	--
Fission Products, Remainder (M'SO ₄)	224.26	5.5	1,240	550	--
(M'(OH) ₄)	165.29	9.6	1,580	--	--
(M'' ₂ O ₃)	296.59	0.7	210	1.16 ^(e)	215
(MO _x ⁻¹)	185.99				
Mo, as Na phosphomolybdate (Na ₃ PO ₄ -12MoO ₃)	1507.94	7.8	980	4.2	500
Mn, as MnO ₂ (est'd)	86.94	25	2,175	--	--
Pu, as PuO ₂		--	35	--	--
U, as Na ₂ U ₂ O ₇	633.98	21.0	6,657	--	--
Actinides, total as oxides	--	19	--	--	--
Totals			98,789		1,203,058
		~28,000 liters			557 g/L
		assumed dry density of 3.5 g/cc			

(a) Based on composite of information from NFS (J. P. Duckworth, private communication), the NFS Waste Surveillance report No. 9-78-09; and calculations based on total MWD burnup in fuel processed at NFS.

(b) Assuming ratio of chromium to nickel to be 19:9 (the ratio in which it occurs in 304 stainless steel).

(c) Average atomic weight - 143.9

(d) (Rb, Cs)NO₃, avg MW 189.52

(e) Technitium as NaTcO₄. It is considered very doubtful that this is present; the Tc is most likely to be present as a Ba pertechnetate, coprecipitated with BaSO₄ (Martin & Miles, "Chemical Processing of Nuclear Fuels," Academic Press 1958; p. 77)

Other commercial firms have become involved in commercial fuels reprocessing to some extent short of operation. A proposed high-level liquid waste composition by the Allied General Nuclear Services⁽⁴⁾ is indicated in Table 6. Other unique liquid wastes highly contaminated with plutonium and radioactivity such as intermediate level liquid waste (Table 6) are generated in a fuels reprocessing plant, and these are usually combined with the high-level liquid wastes except for organics which are handled separately or incinerated.

TABLE 6. Allied General Nuclear Services High-Level and Intermediate-Level Waste Compositions^(a)

	HLLW		ILLW
	Nominal	Minimum	
Fission Products Less I (g/l)	67.67	45.07	
Iodine @ 0.5% (g/l)	0.0032	0.0022	.0043
Uranium @ 0.5% Loss (g/l)	12.69	8.45	16.91
Plutonium @ 0.5% Loss (g/l)	0.117	0.076	0.152
Other Actinides (g/l)	1.75	1.17	0.0035
Soluble Poison (g/l)	64.22	42.77	
Nitric Acid (M)	4-7	4-7	2.5
Total Nitrate @ Max. HNO ₃	10.54	9.25	3.5
Phosphate (g/l)	0.45	0.30	23.0
Shear Fines (g/l)	0.66	0.44	
Corrosion Products (g/l)	0.65	0.43	0.17
Chloride (g/l)	0.053	0.035	0.32
Sodium (potassium) (g/l)			17.64 (0.36)
Manganese (g/l)			0.5
Sulphate (g/l)			0.11
Decay Heat (Watts/l)	3.13	2.51	0.012
Est. Insoluble Solids (g/l)	14.6	9.7	2.0

(a) Bases: Equilibrium fuel aged 3 yr prior to reprocessing.

Government defense wastes are currently being stored on government sites. The sites where the bulk of the waste is stored are Hanford, Savannah River, and the Idaho National Engineering facility. Much of the wastes generated at these sites are related to the fabrication and reprocessing of fuel for defense and development purposes. The high-level wastes at Hanford and Savannah River plants are stored as neutralized slurries in underground tanks. Typical amounts and descriptions⁽⁵⁾ are shown in Table 7.

Defense high level wastes differ from proposed high-level commercial wastes in that the heat and radionuclide content and burnup are much lower for defense wastes. There is also a much wider compositional variation in defense wastes.

Other radionuclide containing wastes such as paper, glass, rags, and used equipment are placed in containers such as 55-gallon drums, wooden or metal boxes, or concrete boxes. These are stored on concrete pads or in shallow land burial. Miscellaneous liquid wastes containing substantial amounts of

TABLE 7. High Level Wastes Stored in the United States⁽⁵⁾

Source Site	Present Form	1978 Quantities		1990 High Estimate	
		10 ⁶ Gal	10 ⁶ Curies	10 ⁶ Gal	10 ⁶ Curies
Rockwell Hanford Operations	Alk. salt/sludge Liquor	50	190	65	230
	Separated ⁹⁰ Sr/Y ¹³⁷ Cs/Ba	-	350	-	425
Idaho Chemical Processing plant	Acid Calcine	0.42	70	1.3	500
	Acid Liquid	2.4		1.2	
Savannah River Plant	Alk. salt/sludge Liquor	23	560	22	680
National Fuel Services	Alk. salt/sludge Liquor	0.6	64	0.6	48
	Acid Liquid	0.01	2.1	0.01	1.6

fission products and/or transuranics such as machining oils, lubricants, organic solvents, and other material processing solutions are currently immobilized as solids for storage.

WASTE FORM OPTIONS

During the past 20 years, numerous waste forms and processes have been proposed for solidification nuclear wastes. The waste forms have ranged from simple concepts such as direct storage of calcine to complex forms utilizing crystalline products, coatings, and metal matrices. The number of options has increased significantly during the past three to four years; as this number increases, so does the difficulty in differentiating the options and making realistic comparisons.

Waste form options for immobilization of high-level wastes can be divided into basic categories as illustrated in Figure 1. The level of development of these waste forms ranges from full-scale demonstration with actual high-level waste, as in the case of borosilicate glass, to lab-scale development with simulated wastes, as for synthetic minerals (SYNROC) and hot-pressed ceramics. Many of the waste forms including glass, glass-ceramics, supercalcine, and concrete have been fabricated containing curium or plutonium to study the effect of alpha-exposure on waste form properties.

The waste form properties of crystalline and glass options have been reviewed by Lutze⁽⁶⁾ and Ross et al.⁽⁷⁾ General conclusions were that either glass or crystalline materials (e.g., glass-ceramic, ceramics) can be shown to have some advantage when a single property is considered. However, the differences are small and each material has both assets and liabilities. With proper design, either type of waste form can almost certainly be utilized to solidify and contain radioactive waste. Jardine and Steindler⁽⁸⁾ compared metal-matrix waste forms. They concluded that metal-matrix encapsulation of commercial solidified waste can serve (1) to increase the thermal conductivity of the waste form, and (2) to produce composites having reduced leach rates and improved mechanical strengths. Rusin et al.^(9,10) have compared several waste

FIGURE 1. Alternative Waste Form Options

forms in assessing the characteristics of metal matrix or multibarrier waste forms. These forms offer some improvements over monoliths but will be more difficult to prepare.

Advances in waste form science with special emphasis on alternatives to glass have been reviewed by a recent National Academy of Sciences Panel on Waste Solidification.^(11,29) Conclusions of the panel relevant to waste form selection are:

- The Panel concludes that solid waste forms should be selected only in the context of the total radioactive waste management system. Considerations affecting this choice include the age of the waste, the hazards involved in processing, the amount of transportation entailed, and the characteristics of the geological formation in which the solid will be emplaced.
- The Panel concludes that defense wastes which are relatively low in radioactivity and thermal power density can best be solidified by low-temperature processes, such as those used to produce cement-matrix and some ceramic forms.
- For solidification of fresh commercial wastes that are high in specific activity and thermal power density, the Panel recommends that, in addition to glass, the use of fully-crystalline ceramics and metal-matrix forms be actively considered.

In addition to waste form properties, waste form process complexity must also be considered in selection of a waste form option. Ross et al.⁽¹²⁾ have reviewed 15 processes and 14 current waste forms in regards to process complexity. They conclude that the simplest processes are cast concrete and spent fuel encapsulation. Processes of high complexity are cermets and coated pellets in a metal matrix. (These could be simplified by combining some of the required processing operations.) In a parametric performance ranking of alternative nuclear waste encapsulants, Hench⁽¹³⁾ has made similar rankings. Calcium-alumina-silicate glass has the highest performance index with cermets and SYNROC being the lowest.

There are many waste forms and process options available for the immobilization of high-level nuclear wastes.^(14,15) One of these options, cast glass, has been under development for many years and is available for near-term utilization, if required. Alternative approaches to cast glass, such as glass marbles, coated pellets, glass ceramics, cermets, synthetic minerals, and concrete formed-under-high-pressure-and-temperature, are relatively new and have received less development than glass. Although glass appears as an acceptable waste form, improvements, particularly in chemical durability, may be offered by alternative waste forms.

Many alternatives have shown considerable promise such as the synthetic mineral concept of SYNROC, the multibarrier approach with coated particles in a metal matrix, and the high pressure-high temperature ceramics. Since these alternatives are "new" concepts in reference to glass, substantial effort for further research and development is required to bring their state of development up to that of glass.

REVIEW OF WASTE FORM DEVELOPMENT IN THE UNITED STATES

The present status of development and a discussion of previous waste form development activities in the U.S. is described in this section. The contents are listed in accord with the seven categories as outlined in Table 1. For reference, activities of major U.S. laboratories in each waste form area are indicated in Table 8.

TABLE 8. Major U.S. Waste Form Development Activities

<u>Laboratory</u>	<u>Glass</u>	<u>Sintered Ceramic</u>	<u>Glass Ceramic</u>	<u>Hot-Pressed Ceramic</u>	<u>Coatings</u>	<u>Concrete</u>	<u>Metal Matrix</u>
ANL							X
Rockwell Hanford	X	X					
ICPP	X	X					X
PNL	X	X	X	X	X		X
SLA		X					
PSU		X		X		X	
LASL		X					
ORNL				X		X	X
SRL	X					X	
BNL						X	

GLASS

Glass provides an alternative to pelletization or direct containment of existing HLW calcines. The glass waste form offers improved durability and can accommodate variation in waste calcines.

Glass waste forms can consist of monolithic shapes or marbles used as a part of a multibarrier concept. Glass is produced by heating mixtures of calcine and glass frit or calcine and glass batch materials at temperatures near 1050°C. The formation of glass by direct liquid feeding to a continuous ceramic melter is also possible. Typical waste glass compositions are illustrated in Table 9. Comprehensive reviews on glass for waste fixation have been presented by Mendel.^(16,17,19)

TABLE 9. Typical Waste Glass Composition

Oxide	Glass Composition, Wt%		
	Borosilicate	Alumina Silicate	Phosphate
SiO_2	25-50	33-40	0-6
B_2O_3	9-22		
P_2O_5	0-2		30-55
Alkali metal oxides	8-19	18-22	5-25
Alkaline earth oxides	0-6	13-16	
Fe_2O_3 , Cr_2O_3 , NiO	1-20		0-30
Al_2O_3	0-10	26-30	0-35
TiO_2	0-3		
ZnO	0-22		
CuO	0-3		
PbO	0-50		0-30
Gd_2O_3	0-12		
Fission products	30	5	30
Actinides	10	1	10

Glass, in the monolithic form, has been considered as a reference nuclear waste immobilization process and waste form by all sites involved in waste fixation. This includes TRU wastes,^(19,20) defense wastes,⁽²¹⁻²⁸⁾ and commercial wastes.⁽³⁰⁻³²⁾ Glass for waste fixation has had over two decades of development and thus is a well established process.⁽³³⁻³⁶⁾ Glass also can accommodate large variations in waste streams due to its random network structure (amorphous or disordered).

Due to the comprehensive amount of literature available on glass for nuclear waste fixation, only current efforts will be reviewed for the major U.S. programs. SRL, INEL and Rockwell Hanford Operation (RHO) are developing glass for their specific defense wastes. PNL in the past has concentrated on proposed commercial HLW but currently is supporting defense and TRU waste glass development. A generic program is also underway at PNL to develop a systematic approach to glass formulation. This program should result in a better understanding of glass formulation and the effect of waste stream variations.

PNL

Glass development and characterization at PNL is well summarized in annual reports.^(37,38) Compositions of reference PNL glasses are given in Table 10. Glasses have been developed for both in-can melting or joule-heated melting. In general, glasses have been formed with simulated waste loadings from 30-50% and density from 3.0 to 3.4 g/cm³. Soxhlet and room temperature pH4 and pH9 leachability ranges from 10⁻⁶ to 10⁻⁷ g/cm²-d. The leach rates of fully-radioactive glass were found to correlate to those of simulated waste glass. The leach rates of Cs and Sr from fully radioactive and simulated glass are 2×10^{-5} g/cm²-d. The leach rate as a function of time for various isotopes in fully-radioactive 72-68 glass is shown in Figure 2. Volatility of simulated waste glasses is from 1 to 2 orders of magnitude better than calcine but 3 to 30 times lower than some crystalline forms. Impact resistance is good in that only 9 wt% fines <37 μ m are released upon impact at 158 ft-lb.

TABLE 10. Reference PNL Waste Glass Compositions(a)

Glass Code Waste Type Frit Code	72-68 PW-4b 73-1	76-68 PW-8a 76-101	77-260 PW-7c 77-269	77-107 PW-9 77-268
SiO ₂	27.3	40.0	36.0	38.0
B ₂ O ₃	11.1	9.5	9.0	13.0
Na ₂ O	4.0	7.5	8.0	2.0
K ₂ O	4.0	--	2.0	4.0
ZnO	21.3	5.0	--	5.0
CaO	1.5	2.0	1.0	2.0
MgO	1.5	--	--	--
SrO	1.5	--	--	--
BaO	1.5	--	--	--
TiO ₂	--	3.0	6.0	3.0
Al ₂ O ₃	--	--	2.0	--
CuO	--	--	3.0	--
Waste	26.3	33.0	33.0	33.0

(a) Weight Percent

FIGURE 2. Leach Rate as a Function of Time for Cs, Sb, Sr, Pu, and Cm in 72-68 Glass

Depending upon glass composition, density changes are $\pm 1\%$ upon accelerated exposure to alpha radiation. No phase degradation or significant physical change is observed at alpha doses equivalent to one million years of exposure. The stored energy released on heating to 600°C measures 20-50 cal/g. Hydrothermal tests on glass indicate results can be obtained equivalent to crystalline products^(7,39) (see p. 81 for more discussion on hydrothermal leaching).

ICPP

Glass development at ICPP is directed towards zirconia-type calcines, the most prevalent type produced.⁽⁴⁰⁾ Disc pelletizing of the calcine is one option to provide a less dispersible, more leach resistant material. Glass is being investigated as an alternative process to disc pelletization. The zirconia calcine waste is unique from other nuclear wastes in that it contains ~ 50 wt% CaF_2 . Over one hundred melts containing simulated zirconia calcine were evaluated to obtain a durable glass that would retain fluoride and have a viscosity below 500 poise at 1050 to 1150°C .

From the development program it was concluded that vitrification of zirconia calcine appears feasible at temperatures (1100°C) which should be practical for remote operation. The glass produced was uniform without observable occlusions. Some fluoride volatility may occur, but an off-gas system similar to that presently used in the ICPP calcining process should be capable of scrubbing the fluoride. The glass selected as optimum contained from 5 to 33 wt% calcine. The calcine was vitrified with addition of a frit containing 66% SiO_2 , 24% Na_2O , 8% B_2O_3 , and 2% CuO . The glass has good ability to vitrify zirconia calcine, and is not sensitive to expected variations in waste content or in waste composition. From 4 to 9% fluorine was lost during melting.⁽⁴¹⁾ Devitrification of the glass does not result in loss of Soxhlet leach resistance. Leach rates in a strong acetic acid solution (pH 3.8) can increase, by up to a factor of 10. Typical Soxhlet leach rates were 10^{-4} to 10^{-5} g/cm²-d.

Rockwell Hanford Operation

One option for long-term management of the Hanford defense wastes involves retrieval of the radioactive wastes from underground storage tanks

and subsequent removal of the long-lived radionuclides from the water-soluble portion of these wastes. The resulting concentrated radionuclides would then be combined with the water-insoluble waste (sludge) and converted to an insoluble silicate glass form suitable for long-term storage or disposal. The bismuth phosphate, uranium recovery, Redox and Purex processes generated sludges characteristic of their different process chemistries. The chemical compositions of such wastes are thus highly varied and pose unique problems to development of suitable glass formulations for their fixation.

Development of glass forms for fixation of Hanford defense wastes is being conducted by (RH0).⁽²⁵⁻²⁷⁾ Borosilicate-type glass formulations were evaluated for fixation of synthetic sludges. Sodium-borosilicate and soda-lime compositions were evaluated for fixation of residual liquid wastes. Because of the superior leach resistance of most high-melting glasses, high temperature (1200 to 1400°C), as well as low-temperature (1000 to 1200°C) glass formulations were tested. Tables 11 and 12 list conditions and results of selected vitrification experiments.⁽⁴²⁾

Glasses made from residual liquid and Purex process sludges do not devitrify appreciably when cooled (3°C/hr) from 1000°C to 400°C. Redox sludge glasses that have been cooled by air quenching normally contain inclusions (~2 vol %) of Cr_2O_3 . Leach rates of the devitrified specimens are no higher, however, than those of the original glasses. Waste forms incorporating BiPO_4 and Uranium Recovery process sludges devitrify when cooled slowly, but are vitreous if cooled rapidly.

About 0.5 to 2.0% and 0.02 to 0.5% of the cesium in residual liquid and sludge wastes, respectively, volatilizes when the waste-glass batches are melted in crucibles. Because of the high content of nitrites and nitrates in residual liquid waste, considerable foaming occurs during melting.

Vitrification tests with actual Redox and Purex process sludges and residual liquids have been performed. The products have exhibited properties similar to those prepared from synthetic wastes.

TABLE 11. Vittrification of Hanford Sludges

Sludge Type	Waste Oxides	Composition, wt%				Temperature (for viscosity 50-250 poise), °C	Soxhlet Leach Rate, (b) 10 ⁻⁴ g/cm ² -d	Loss, wt%		
		Frit(a)	Li ₂ O	ZrO ₂	Al ₂ O ₃			Soxhlet	Acid	Alkali
Purex	30	70	--	--	--	1250	0.9	2.2	0.40	1.2
	30	68	2	--	--	1150	1.6	4.5	0.83	1.2
Redox	25	73	2	--	--	1400	0.1	0.90	2.1	0.90
	25	70	5	--	--	1200	0.6	2.2	5.4	1.4
BiPO ₄	50	45	--	5	--	1300	2.8	2.0	0.08	1.1
	50	43	2	5	--	1200	3.6	3.0	0.19	1.4
BiPO ₄ (3rd cycle)	30	65	--	--	5	1350	0.7	0.81	0.14	1.5
	30	60	5	--	5	1150	2.0	1.8	0.21	1.8
Uranium Recovery	30	70	--	--	--	1300	5.2	12.0	0.40	1.0
	30	63	2	5	--	1200	2.2	5.9	0.42	1.4
Total for: Commercial Borosilicate Glass								0.20	0.08	2.4
Commercial Soda-Lime Glass								4.1	0.10	0.6

(a) Frit composition, wt%: 13 Na₂O; 11 B₂O₃; 76 SiO₂.

(b) Leach rate at 100°C based on cesium. The crushed glass particles used for the soxhlet test are assumed to be spherical which leads to a calculations of minimum surface area. Thus, leach rates noted in the table are believed maximum values.

TABLE 12. Vitrification of Hanford Residual Liquid

Waste Oxides(a)	Ingredients, wt%						Temperature (for viscosity 50-250 poise), °C	Soxhlet Leach Rate,(a) 10 ⁻⁴ g/cm ² -d	Loss, wt%		
	SiO ₂	B ₂ O ₃	Li ₂ O	TiO ₂	CaO	Al ₂ O ₃			Soxhlet	Acid	Alkali
Vitrification of Residual Liquid											
25	60	10	--	5			1200	0.4	0.60	0.07	2.3
25	58	10	2	5			1100	0.9	1.3	0.14	1.5
Vitrification of Radionuclide Removal - Processed Residual Liquid											
20	65	10	--		--	5	1300	0.5	1.2	0.08	0.71
20	65	10	2		--	5	1200	0.9	2.4	0.37	2.3
20	63	--	2		10	5	1300	1.3	2.5	0.15	0.50

(a) Frit composition, wt%: 13 Na₂O; 11 B₂O₃; 76 SiO₂.

From the studies it was concluded that Hanford sludges and residual liquids can be effectively immobilized by conversion to silicate glasses. Because of the high variability of the compositions of Hanford wastes, glass formulations must be tailored somewhat to provide glasses exhibiting the desired physical and chemical properties. Some compromise in chemical durability must be made to obtain low-melting glasses. Future work at (RHO) will be centered on further refinements of glass compositions and detailed physical and chemical characterization of the products.

SRL

Radioactive waste at the Savannah River Plant contains high concentrations of nonradioactive compounds of iron and aluminum. Borosilicate glass is being evaluated for use as a matrix to immobilize the SRP high-level radioactive waste sludges.⁽⁴³⁾ Glass development studies at SRP have centered on determining the effect of iron and aluminum on melt properties for two processes: in-can melting and joule-heated melting. Viscosity, resistivity, volatility, and leachability are important parameters that are determined. For in-can melting, viscosity of ≤ 200 poise at melt temperature is necessary. To produce an acceptable product by joule-heated melting, a viscosity of ≤ 50 poise at the melting temperature is necessary. In addition, a viscosity of ≤ 500 poise is necessary for smooth pouring.

SRP sludges are generally high either in iron, aluminum, or both which can cause processing problems. Sludges containing large amounts of Fe_2O_3 produce crystals of a ferrite-spinel type when vitrified. At high concentrations, these crystals cause the melts to become non-Newtonian (apparent viscosity depends on shear rate) pseudoplastic fluids.⁽²⁹⁾ However, even at low concentrations, an extremely viscous layer gradually forms at the bottom of a joule-heated melter. This layer disrupts smooth operation of the melter and plugs narrow channels. Sludges containing large amounts of Al_2O_3 make extremely viscous melts, which readily devitrify to alkali aluminosilicates. Such sludges might require special processing to produce an acceptable product. Resistivity also increased with addition of high aluminum or high iron

sludge.^(44,45) Four methods have been identified for handling these extremes in composition:

- Increasing the temperature of the melt
- Reducing the waste loading
- Blending sludges
- Changing frit composition

The effects of several glass composition variables on these processing problems have been investigated.⁽⁴⁴⁾ The most important variables were the TiO_2 content, the molar alkali-to-silica ratio, and the molar ratio of Li_2O to total alkali. As the TiO_2 content decreases, the amount of crystalline material (either ferite-spinel or aluminosilicate) also decreases. However, the viscosity of the melt increases. Increasing the alkali-to-silica ratio and the Li_2O to total alkali ratio decreased the viscosity greatly, but also increased the tendency to devitrify. Other variables investigated were MO content ($M = \text{Mg, Ca, Ba, or Cu}$) and R_2O_3 content ($R = \text{Al or B}$). None of these variables were of major importance. Composition of the glass forming frit is given in Table 13. Glasses were prepared typically containing 25% sludge although waste loadings of 40% were achieved. Product density was $\sim 3.00 \text{ g/cm}^3$. Initial leach rates for ^{137}Cs and ^{90}Sr were $10^{-6} \text{ g/cm}^2\text{-d}$ for tests made at room temperature in pH4, pH9, and pH7.⁽⁴⁶⁾ The leachability of devitrified glass can be up to 100 times greater than the leachability of as-cast glass as shown⁽⁴⁷⁾ in Table 14. Volatility for Cs was $<0.5\%$ at 1150°C for 3 hours and for Ru, 7%

TABLE 13. Composition of SRL Glass-Forming Frit^(a)

Component	Amount (wt%)
SiO_2	52.5
Na_2O	18.5
Li_2O	4.0
B_2O_3	10.0
TiO_2	10.0
CaO	5.0

(a) Borosilicate Glass Mix 18

TABLE 14. Comparison of Leachabilities of Heated and Unheated Waste Glasses^(a)

Sample	Unheated	500°C	600°C
	⁹⁰ Sr Leachability (g/cm ² -d)		
40 wt% SRP Tank 5	2.2 x 10 ⁻⁷	7.0 x 10 ⁻⁶	5.0 x 10 ⁻⁶
40 wt% SRP Tank 13	4.4 x 10 ⁻⁷	6.4 x 10 ⁻⁶	4.3 x 10 ⁻⁶
30 wt% SRP Tank 13 (10 wt% zeolite)	1.2 x 10 ⁻⁷	2.1 x 10 ⁻⁶	--
	¹³⁷ Cs Leachability (g/cm ² -d)		
40 wt% SRP Tank 5	5.9 x 10 ⁻⁸	1.7 x 10 ⁻⁸	1.0 x 10 ⁻⁷
40 wt% SRP Tank 13	3.5 x 10 ⁻⁸	3.1 x 10 ⁻⁷	4.8 x 10 ⁻⁶
30 wt% SRP Tank 13 (10 wt% zeolite)	5.6 x 10 ⁻⁸	2.7 x 10 ⁻⁸	--
	Gross Alpha Leachability (g/cm ² -d)		
40 wt% SRP Tank 13	1.3 x 10 ⁻⁷	6.0 x 10 ⁻⁸	2.7 x 10 ⁻⁷
30 wt% SRP Tank 13 (10 wt% zeolite)	--	6.1 x 10 ⁻⁸	--

(a) Heated 1 month.

at the same conditions. Glasses doped with ²⁴⁴Cm showed positive dilation of 0.005 ΔV/V at an α-dose of 4 x 10¹⁰ Rads.

SINTERED CERAMIC

Calcine may be mixed with glass frits, clays, and other minerals and consolidated by subsequent heat treatment. The resultant product is primarily crystalline with some amorphous phases present. The process may involve a pressing operating or disc pelletization for initial consolidation before heat treatment.

A form of sintered ceramic, termed crystalline product, has been developed by RHO.⁽⁴⁸⁾ The crystalline product is formed by pressing a mixture of dry powders or precipitated sludge, clay, binder, and water. Crystallization takes place by sintering between 1150 and 1350°C. Both crystalline and amorphous phases are present in the final product. Soxhlet and room temperature leach resistance ranges from 10^{-4} to 10^{-6} gm/cm²-d. Density ranges from 2.1 to 2.4 g/cm³ at waste loadings of 39 to 90%.

Pelletized sintered ceramics have been developed at ICPP^(49,50) for simulated zirconia calcine. Liquid binders including water, phosphoric acid, nitric acid, colloidal silica (Ludox), and alumina (aluminum phosphate) were evaluated. Phosphoric acid and mixtures of phosphoric and nitric acid were superior. Solid binders such as bentonite, metakaolin, boric acid, and Ca(OH)₂ were tested. Small amounts, 2 to 5 wt%, of bentonite, metakaolin, and boric acid were beneficial to pellet handling and leach resistance. Pellets 3 to 10 mm were prepared with a bulk density of 1.0 to 1.4 g/cm³. Bulk Soxhlet leachability was 10^{-4} to 10^{-5} g/cm²-d and Cs leachability was 10^{-3} gm/cm²-d. Compressive strength ranged from 3 to 6 MPa, (400-900 psi) and waste loadings ranged from 70 to 90%.

Sintered ceramics were first investigated at PNL by Ross.⁽⁵¹⁾ Mixtures of 30 to 65 wt% spray calcine and glass frit were formed into pellets by cold pressing at 10,000 psi followed by sintering at 675°C. Densities of 3.05 g/cm³ with 10% porosity were obtained. A later program at PNL⁽⁵²⁾ evaluated several additives including SiO₂, glass frit, bentonite, kaolin, feldspar, and mineral colloid. Pressures of 600 psi and temperatures from 600 to 1000°C were used. Densities from 2.6 to 3.2 g/cm² were obtained for waste loadings of 50 and 33 wt%. Present efforts in sintered ceramics are fabrication of a glass frit sintered ceramic containing 50 wt% simulated HLW (PW-9) for the PNL comparative study.

Crystalline waste forms are very applicable for the immobilization of a single waste ion, such as cesium, since variation in waste stream does not need to be considered. Pollucite, CsAlSi₂O₆, is found in nature and has promising waste form stability. Radiation effects, such as transmutation of Cs to Ba and metamictization (transition from crystal to glass) may be the limiting

parameters. Pollucite sintered ceramics have been developed at RHO⁽⁵³⁾ and SLA.⁽⁵⁴⁾ Mixtures of either cesium and clay or $\text{CsCO}_2\text{-Al}_2\text{O}_3\text{-SiO}_2$ (Ludox) were used.

The additives may be added directly to the liquid waste stream before calcination such as in the case of supercalcine. Supercalcine is formed by the addition of certain additives such as SiO_2 , CaO , Al_2O_3 , and SrO to the nitrate liquid waste stream followed by spray calcination. The supercalcine ceramic is produced by consolidation and heat treatment between 950 to 1200°C. The resultant product is primarily crystalline with some glass phase. A typical phase formation model for supercalcine is shown on Table 15. For high sodium wastes the sodalite phase, $(\text{Ca}, \text{Sr}, \text{Ba}) [\text{NaAlSiO}_4]_6 \text{MoO}_4$ is formed instead of Na-pollucite and scheelite.

Supercalcine has been formed as cold pressed and sintered, and hot pressed or hot isostatic pressed simulated waste pellets. Kilogram quantities have been produced by disc pelletization and sintering. Radiation damage has been determined by ^{244}Cm doping.

TABLE 15. Primary Containment Phases in Current Supercalcine-Ceramics

HLW Ions ^(a)	Primary Containment Phases	Structure Type
Sr, Ln ^(b)	$(\text{Ca}, \text{Sr})_2 \text{Ln}_8 (\text{SiO})_6 \text{O}_2$	Apatite
Ln, $[\text{PO}_4]$	LnPO_4	Monazite
Cs, Rb, Na	$(\text{Cs}, \text{Rb}, \text{Na}) \text{AlSi}_2 \text{O}_6$	Pollucite
Sr, Ba	$(\text{Ca}, \text{Sr}, \text{Ba}) \text{MoO}_4$	Scheelite
U, Ce, Zr	$(\text{U}, \text{Ce}, \text{Zr} \dots) \text{O}_{2+x}$	Fluorite
Zr, Ce, U	$(\text{Zr}, \text{Ce}, \text{U} \dots) \text{O}_{2+x}$	Tetragonal-Fluorite
Fe, Ni, Cr	$(\text{Ni}, \text{Fe}) (\text{Fe}, \text{Cr})_2 \text{O}_4$ and $(\text{Fe}, \text{Cr})_2 \text{O}_3$	Spinel Corundum
Ru	RuO_2	Rutile

(a) Te, Pd, Rh, Tc, Pm, Np, Pu, Am, Cm were not included in the simulated waste.

(b) Ln = La, Pr, Nd, Sm, Eu, Gd, Y.

(c) Additive ions were underlined.

The properties of supercalcine ceramics have been determined. Soxhlet, pH-9 and pH-4 leachabilities range from 10^{-5} and 10^{-7} g/cm²-d for hot pressed supercalcine. Impact resistance of hot pressed supercalcine is a factor 2 greater than that of a glass monolith. Volatility of supercalcine is less than glass by a factor of 3 to 30 depending upon temperature and formulation. Density ranges from 2.2 to 4.8 g/cm³ and waste loadings from 65 to 80%. There is a 1.5% density decrease and loss of apatite phase after an equivalent alpha-exposure of 200 yr. Stored energy measured up to 600°C is 10 cal/g.

A third type of sintered ceramic is formed by absorption or ion exchange of the liquid waste stream onto a ceramic substrate which is subsequently heat treated. The ceramic sponge process developed by LASL⁽⁵⁵⁾ and the titanate ceramic developed by SLA⁽⁵⁶⁾ are examples.

In the ceramic sponge process, liquid simulated waste is absorbed on a clay-ceramic body (bisque fired). The clay-ceramic is dried and fired at 1200 to 1300°C. The product had low Cs but high Ru volatility during firing. Leachabilities for Cs and Sr were low. Waste loading was not specified but from the process description must be very low.

In the titanate ceramic process, sodium-titania-based gels are used as inorganic ion exchangers for simulated high-level liquid waste ions. The loaded titanate ion exchanger is dried and hot pressed at 6.9 MPa and 1100°C into crystalline dense ceramics. Typical composition of titanate ceramics are 25 wt% waste, 62.9% TiO₂, 2.1% Si, and 10% Zeolon 900. Primary phases have been identified as described in Table 16. Similar results were obtained after heat treatment at 1200°C for 19 hr. Long-term heat treatment at 800°C for 475 hr in air showed two distinct zones on the sample periphery with cesium and rubidium depletion. Thus, volatility of this product warrants further investigation. The hydrothermal leach resistance of titanate ceramics is better than glass waste forms.⁽⁵⁷⁻⁵⁹⁾ The final product has a bulk density of 4.1 to 4.3 g/cm³ and waste loading of 22 to 25%. Porosity is <1 vol%. The thermal conductivity is about twice that of borosilicate glass.

TABLE 16. Primary Containment Phases Identified(a)
in SLA Titanate-Ceramics

<u>Phase</u>	<u>Energy Dispersive Elemental Analysis</u>	<u>Est. Vol. Fraction</u>
TiO ₂ (Rutile)	Ti	50%
Amorphous Silica (SiO ₂)	Si (trace U, Ti, Al, Na)	5%
Cs ₂ O·Al ₂ O ₃ ·4SiO ₂ (dehydrated pollucite)	Si, Al, Cs (Trace Ti, Rb)	1%
Gd ₂ Ti ₂ O ₇ (Some U, Nd) (Trace Zr, Y)	Ti, Gd	10%
Elemental Mo	Mo (Trace Fe, Ti)	5%
Elemental Pd	Pd (Some Te and Ti) (Trace Fe, Mo)	2%
Cubic-ZrO ₂	Zr (Trace U, Si)	5%
Amorphous Zeolite, (Na, Cs) Alumino- Silicate	Na, Cs, Al, Si (Trace Ti, U, Fe, Mo, Gd, Sr)	10%

(a) At least eight more distinct phases have been detected by electron diffraction and/or x-ray energy dispersive analysis. These have not been identified, but most appear to be titanates.

GLASS CERAMIC

Glass waste forms of proper formulation can be converted to a mixture of crystals and glass (i.e., a glass ceramic) by a heat treatment process involving nucleation and crystal growth. Some improvement in stability parameters may be obtained but this is dependent upon the amount of residual glass phase which can approach 50%. Glass ceramics are formed by the same methods as those used for glass and thus may be in the form of monoliths or marbles.

Glass ceramic samples containing simulated waste calcine are being fabricated and characterized at PNL based upon the HMI celsian glass ceramic formulation.⁽⁶⁰⁾ The samples contain 20 wt% simulated waste calcine (PW-9). The celsian glass ceramic will be included in the PNL comparative study for comparison to other waste forms. For reference see discussions on HMI glass ceramics and the ANU SYNROC A, which is a form of a glass ceramic (recrystallized fusion melt). Studies have also been initiated at PNL to develop a waste form based upon the composition of basalt. Hanford basalt has been mixed with 20 wt% simulated waste calcine (PW-9) and melted at 1400°C. The initial glass product can be crystallized by proper heat treatment. Basalt glass ceramics developed by Corning Glass Works^(61,62) have demonstrated durability better than that of the parent rock in both acid and alkali leach tests.

HOT PRESSED CERAMICS

Dense ceramic waste forms may be produced by hot pressing (pressing uniaxially at high temperatures and pressures) or by hot isostatic pressing, HIP, (uniform pressure applied in all dimensions at high temperatures). These waste forms may contain 100% calcine but normally contain 10 to 50% additives such as glass frit, clays, or minerals. Potential problems may exist in the remote operation of such high pressure and temperature processes.

Simulated waste calcine (PW-9) has been hot pressed for studies at PNL.⁽⁵²⁾ The samples were pressed at 5000 psi at temperatures ranging from 800 to 1000°C. The resultant densities, as shown in Table 17 ranged from 3.6 to 4.2 g/cm³. It is interesting to note that cold pressed calcine (PW-9) sintered at 1000°C has a density of only 3.18 g/cm³. Thus, hot pressing increases the density by 33%. McCarthy⁽⁶³⁾ hot pressed mixtures of quartz, lead borosilicate glass, and simulated waste calcine (PW-4b) at 3000 psi and temperatures between 1000 and 1200°C. Densities from 3.0 to 3.1 g/cm³ were obtained with Soxhlet leachability ranging from 0.8 to 2.7 wt% loss in 72 hr.

Supercalcine formulations for simulated PW-7 waste streams have been hot pressed at temperatures from 900 to 1200°C and 3000 psi.⁽⁵²⁾ Densities from 3.95 to 4.56 g/cm³ have been obtained, as shown in Table 17. Some samples contained voids which may have been caused by trapped gases.

TABLE 17. Density of Hot Pressed Ceramics

A. PW-9 Calcine Pressed at 5000 psi

<u>Temperature,</u> <u>°C</u>	<u>Time,</u> <u>Min.</u>	<u>Density,</u> <u>g/cm³</u>
800	14	3.92
825	14	3.58
875	26	3.79
1000	105	4.22

B. Supercalcine (SPC-4) Pressed at 3000 psi

<u>Temperature,</u> <u>°C</u>	<u>Time,</u> <u>Min.</u>	<u>Density,</u> <u>g/cm³</u>
900	75	3.95
1000	45	4.30
1100	40	4.56
200	30	4.32

HIP tests have also been conducted on simulated waste calcine (PW-9) and supercalcine by BCL for evaluation at PNL.⁽⁵²⁾ Stainless steel containers were used to contain the powder. Process temperature and pressure were 900°C and 30,000 psi. The containers containing calcine showed excessive shrinkage which resulted in some cracking of the containers. The supercalcine containers were intact. Outgassing of residual nitrates and water in spray calcine is a major problem with the HIP process. Work is continuing to produce HIP samples 2 to 6 in. in diameter. These include producing a waste form with an alumina outer layer and supercalcine inner core (similar to ASEA HIP process).

Improved stability parameters can be obtained from concrete if high process temperatures and pressures are used, (see section on concrete for discussion of conventional concrete waste forms). One concept utilizes an autoclave to achieve these conditions. This concept has been given the acronym FUETAP (Formed Under Elevated Temperature and Pressure).⁽⁶⁴⁾ Hot pressing may also be used as demonstrated by Roy.⁽⁶⁵⁾

The FUETAP concept was developed at ORNL.^(64,66) In this concept, cementitious solids are formed at $\leq 250^{\circ}\text{C}$ and < 6.9 MPa (1000 psi) containing simulated radioactive wastes. This concept is unique in that less stringent temperatures and pressures than previous studies⁽⁶⁵⁾ are used and specific additives, as in the case of hydrofracture grouts are added to fix the radio-nuclides.

FUETAP samples with compositions given in Table 18 were prepared containing a simulated Nuclear Fuel Services waste sludge by curing for 24 hr at 240°C and 600 psi. The pressure was applied by use of an autoclave instead of hot pressing. Three cement types were studied: Portland Type I, Atlas Type III, and Universal Atlas HAC-Lumnite. Physical property measurements made on specimens prepared with Type I Portland cement are shown in Table 19. Sufficient data have not been collected in the initial leach tests to establish any definite leach mechanism. A diffusion coefficient for cesium ranges from $10^{-15} \text{ cm}^2/\text{sec}$ into distilled water or spring water to $10^{-13} \text{ cm}^2/\text{sec}$ into Sandia brine. Strontium is more leachable, with diffusivity values ranging from 10^{-11} to $10^{-10} \text{ cm}^2/\text{sec}$. There was essentially no plutonium leached into spring

TABLE 18. FUETAP Mix Composition

Component	Composition, wt%			
	Mix 1	Mix 2	Mix 3	Mix 4
Cement	37.54	38.94	23.24	27.55
Indian red clay	8.94	9.27	8.94	8.94
Fly ash	8.94	9.27	23.24	22.51
Simulated sludge	14.30	14.83	14.30	10.00
Quick-gel	0.41	0.42	0.41	0.40
NaNO_3	2.60	-0-	2.60	2.60
Water	27.27	27.27	27.27	28.00
Mixed ratios				
Fly ash/cement	0.24	0.24	1.0	0.82
Water/fly ash and cement	0.59	0.59	0.59	0.56

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1100	40	4.56
200	30	4.32

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Quick-gel	0.41	0.42	0.41	0.40
NaNO_3	2.60	-0-	2.60	2.60
Water	27.27	27.27	27.27	28.00
Mixed ratios				
Fly ash/cement	0.24	0.24	1.0	0.82
Water/fly ash and cement	0.59	0.59	0.59	0.56

TABLE 19. Effect of Mix Composition on FUETAP Concrete

Mix No. (a)	Compressive Strength (b)		Thermal conductivity, W/cm ⁰ K (x10 ³)	Porosity, %	Density, g/cm ³
	kg/cm ²	(psi)			
1	145	(2060)	4.4	47.6	1.56
2	134	(1900)	4.6	51.4	1.54
3	190	(2700)	4.9	39.4	1.75
4	299	(4250)	5.1	40.1	1.76

(a) All mixes were made with Type I Portland cement. Specimens were cured at 42.2 kg/cm² (600 psi) and 250°C, including the 1.5 hr required to reach curing conditions.

(b) Pressure required to crush a right-circular cylinder 4.8 cm dia by 10.2 cm.

water in the three months the tests have been in progress indicating an order of diffusivity that is 10^{-19} cm²/sec. However, the data suggest that corrosion may be taking place in the distilled water test.

Workers at the Pennsylvania State University have encapsulated simulated PW-4b, PW-4c, PW-6, and calcined PW-6 in cement cylinders using hot-pressing techniques.⁽⁶⁷⁻⁶⁹⁾ The hot-pressing operations were performed at pressures ranging from 25,000 to 100,000 psi and temperatures from 150 to 400°C. Hot-pressed cement products possess properties superior to those of normally hydrated and cured concrete. Interconnecting porosity is virtually eliminated with the samples containing ~3% closed porosity, compared to 20 to 30 vol% porosity in ordinary concrete forms. The main advantages of hot-pressed cement over normal concrete for the isolation of radioactive waste include:

- Compressive strengths of 35,000 psi
- Lower water content (less potential for radiolytic gas generation)
- Lower leachability
- Increased thermal conductivity and thermal stability

Samples containing PW-4c and Fondu (40% Al₂O₃) cement, hot pressed at 50,000 psi for 30 min at a temperature of 150°C, exhibits decreases in strength with increasing waste content. This relationship is depicted in Figure 3.

FIGURE 3. Splitting Tensile Strength of Hot-Pressed Cement Containing PW-4c

Although strength reductions were considerable with 50% PW-4c content, overall strengths for all formulations are vastly superior to normally hydrated and cured concrete waste forms.⁽⁷⁰⁾ Hot-pressed cement samples prepared with Fondu cement and 40% PW-4c exhibit compressive strengths on the order of 20,000 psi, compared to ~5,000 psi for normally cured samples of HAC plus 40% simulated SRP sludges. Thermal shock resistance of hot-pressed samples was tested by immersion of samples heated to 760°C in cold water; no signs of cracking or disintegration was evidenced. Furthermore, heating of Fondu cement plus 20% PW-6 at 230°C causes an initial strength increase up to 24 hr, followed by a gradual decrease through 28 days.⁽⁷¹⁾

The lower water content of hot-pressed cement samples, generally about 30% of that required for normally hydrated and cured cement pastes, allows the production of high strength, high density products. Leachability and volume stability are expected to be superior to ordinary cement pastes because of the absence of interconnecting porosity within the hot-pressed samples. Thermal conductivity also increases with increasing density.

COATINGS

Coatings may be applied to the previously reviewed waste forms to enhance leach resistance, mechanical strength, and/or thermal stability. The coatings may consist of conventional ceramics such as Al_2O_3 or SiO_2 ; carbon products such as pyrolytic carbon, PyC, Cr_7C_3 , or SiC; glass such as borosilicate or aluminosilicate glasses; or metals such as Ni, Si, or Fe.

The CVD technology for application of coatings to calcine and supercalcine particles was primarily developed at Battelle, Columbus Laboratories (BCL) under contract to PNL. Besides this major work at BCL, several preliminary coating evaluations were conducted at General Atomic Company, Oak Ridge National Laboratory, BCL, and PNL as early as 1973. The substrate materials used were spray-calcined simulated waste and alumina particles coated with simulated waste in a fluidized-bed calciner. Substrate particle size ranged from 100 to 300 μm .

Coating studies at General Atomic Company produced PyC and PyC/SiC coatings by CVD in a fluidized bed. Coating thicknesses varied from 10 μm to

120 μm .⁽⁷²⁾ Temperatures of 900 to 1100°C were required for application of PyC coatings by methane and 1100 to 1350°C were required for SiC coatings by silane. The coated particles demonstrated good bonding, high strength, and excellent leach resistance.^(73,74) The high temperature for SiC deposition was a major disadvantage, considering potential radionuclide volatilization during processing. The calcine also displayed some reduction due to the PyC.⁽⁷⁴⁾

The coating studies at Oak Ridge National Laboratory involved the application of PyC on spray-calcined simulated waste. Coatings of good integrity were produced by starting at 850°C with acetylene and then switching to a mixture of methyl acetylene and propadiene at 1150°C.⁽⁷⁶⁾

In addition to PyC and SiC, technology for CVD of several other materials had been demonstrated by BCL. Thus, candidate materials in addition to PyC and SiC were selected for evaluation as coatings for the multibarrier concept. A primary requirement considered for selection of candidate materials was to achieve lower coating temperatures while maintaining resistance to air oxidation and attack by leaching media. Adaptability to large-volume production operated remotely in a hot cell and economics were also considered.

Candidate coating materials produced by chemical vapor deposition in a fluidized bed (CVD/FB) were investigated by BCL.⁽⁷⁶⁾ Table 20 identifies the coatings that have been successfully applied along with some process data. Chromium dicumene and trichlorosilane vapor reacted with the simulated waste particles. Thus, a barrier coating of nickel was required before chromium carbide or silicon coatings could be applied. Although the PyC, Ni/Cr₇C₃, and SiO₂ coatings appeared to be the best, the coating uniformity, integrity, and overall structure in the batches were not of the high quality characteristically obtained by a CVD/FB process. A one-week heat treatment of the Ni/Cr₇C₃-coated material resulted in some degradation at 500°C and almost total destruction of the coatings at 800°C.⁽⁷⁷⁾

PNL investigated the feasibility of applying a protective coating by plasma spraying individual particles.⁽⁷⁷⁾ Simulated waste-glass frit pellets were prepared by cold pressing and sintering. The pellets were right circular

TABLE 20. Coatings Applied in a Fluidized Bed to Particles in the 200- μ m Range

<u>A. Single Coatings</u>		
<u>Coating</u>	<u>Reactants</u>	<u>Deposition Temperature °C</u>
Ni	Ni(CO) ₄	170 to 230
Mo/MoC	Mo(CO) ₆	350 to 450
C	C ₂ H ₂	800 to 950
Fe	Fe(CO) ₅	180 to 200
Si	SiHCl ₃ +H ₂	500 to 800
Cr ₇ C ₃	Cr(C ₉ H ₁₂) ₂	500
SiC	CH ₃ SiCl ₃ +H ₂	1100
Cr ₂ O ₃	CrO ₂ Cl ₂ +H ₂ O+H ₂	550 to 650
SiO ₂	SiCl ₄ +H ₂ O+H ₂	700 to 800
Al ₂ O ₃	AlCl ₃ +H ₂ O+H ₂	600 to 900

B. Duplex Coatings^(a)

Cr₇C₃/Ni

Ni/C₇C₃

Al₂O₃/C

Fe/Al₂O₃

Ni/Si

C/SiC

C/Al₂O₃

(a) Duplex coating -- first material listed was applied to uncoated waste particle -- all materials were deposited by appropriate systems listed in Part A above.

cylinders with curved ends, about 2.5 cm long and just over 2.5 cm in diameter. Initially, pellets were sprayed at room temperature. A Ni/Cr base coat was applied without any problem, but when separate Al_2O_3 and chromium carbide coatings were applied at higher temperatures, the pellets disintegrated. A second plasma spray coating attempt was made with Al_2O_3 and pellets preheated at 500°C . Successful Al_2O_3 coatings were applied to pellets with a Ni/Cr base coat and even to those without a base coat. The preheating eliminated the failure caused by thermal shock.

In summary, several metal, oxide, and carbide coatings were applied to simulated waste particles. The best quality coatings, particularly in terms of high-temperature (up to 1200°C) behavior, were the PyC coatings. Al_2O_3 coatings also looked encouraging although the necessary quality had not been achieved. Though initial results suggested that PyC was perhaps the best coating material in terms of leach protection, it was also considered that it might be desirable to provide oxidation protection for the PyC with an overcoating of Al_2O_3 . Before subsequent BCL studies of such duplex coatings, it also became apparent that disc pelletizing was a better way to produce pellets suitable for coating than was the fluidized bed calciner. With this in mind, CVD coating development at BCL was directed toward the application of PyC and high-quality coatings to pellets 1 mm and larger.⁽⁷⁸⁾

The development efforts at BCL resulted in the CVD coating of ~ 3 kg of 2 mm supercalcin pellets with ~ 40 μm of PyC and ~ 60 μm of Al_2O_3 . A fluidized-bed coater was used with a bed diluent of 0.5 mm ZrO_2 particles for the PyC CVD coating. A vibrating-bed technique was utilized for Al_2O_3 CVD coating via the $\text{H}_2 + \text{CO}_2$ reaction: $3\text{CO}_2 + 3\text{H}_2 + 2\text{AlCl}_3 \rightarrow \text{Al}_2\text{O}_3 + 6\text{HCl} + 3\text{CO}$. Autoclave leach tests for the duplex (PyC- Al_2O_3) coated particles have indicated no release of simulated waste ions in either brine or de-ionized water at temperatures from 350 to 400°C for several weeks.⁽⁷⁹⁾

CONCRETE

The use of cements to form concretes for incorporating solid or liquid wastes has received widespread attention in the management of radioactive wastes.^(80,65,68) Concrete is a mixture of hydraulic cement, water, and

aggregate. Concrete-waste forms may contain calcine or supercalcine as the aggregate or can incorporate waste sludge. Numerous types of low-level radwastes have been considered for solidification in concrete.⁽⁸¹⁾ Potential problems exist for solidification of high-level wastes in concrete due to the radioactivity and radioactive decay heat of the waste. Concrete materials are also generally porous and may break rather easily owing to atmospheric conditions. Proposed post treatments consist of impregnating the concrete matrices with a polymer material.⁽⁸²⁾ The durability of polymer impregnated concrete is improved over that of cement concrete.

Most of the concrete-waste form fabrication and characterization has or is being conducted on low-level wastes. Lokken⁽⁸¹⁾ provides a comprehensive review of studies conducted on low-and intermediate-level and defense high-level wastes. He made the following conclusions from his study:

Use of hydraulic cements for the solidification of various low heat generating wastes was shown to produce products with acceptable properties. However, high heat generating rates (~ 9.2 kW/MTU) and high radioactivity levels ($\sim 1.6 \times 10^6$ Ci/MTU) of HLW appear to have detrimental effects on the feasibility assessment of concrete waste forms. More elaborate offgas and cooling facilities are required during processing because of possible radiolytic gas production and water vaporization. Hot-pressed cement appears a more attractive mechanism for HLW immobilization because of improved physical properties and reduced material requirements. The overall feasibility, however, is governed by processing complexity.

Properties of a concrete matrix for fixation of SRP waste have been studied by Stone.⁽⁸³⁾ Simulated and actual SRP sludge wastes were studied using six types of cements. Leachability for ^{90}Sr , ^{137}Cs , and alpha-emitters ranged from 10^{-7} to 10^{-5} , 10^{-4} to 10^{-3} , and 10^{-8} g/cm²-d, respectively. Short set times and possible gas generation were listed as possible disadvantages of the process.

Intermediate-level wastes are currently being immobilized at ORNL⁽⁸⁴⁾ by shale fracturing (often referred to as hydrofracture grout). The waste solutions are mixed with cement and other additives. The resulting grout is then injected into impermeable shale formations at a depth of 700 to 1000 ft. A few hours after injection the grout sets. Pottery clay is added to fix

cesium, drilling clay to retain excess water, and fly ash to fix strontium. Leach resistance equivalent to borosilicate glass has been obtained.⁽⁸⁵⁾

ORNL is currently evaluating solutions to eliminating release of free water with temperature rise and radiolysis. Two potential solutions are heating at 250°C for 15 to 18 hr and utilizing additives that have good catalytic properties in recombining hydrogen and oxygen. These approaches may allow the use of concrete for higher levels of wastes.⁽⁸⁶⁾

The use of additives in concrete grouts as demonstrated in the ORNL shale fracturing has suggested the idea of a supergrout analogous to the use of additives to calcine to form supercalcine.⁽⁶⁸⁾ Cesium leachability from grouts is greatly reduced by additives as shown on Figure 4. Roy et al.⁽⁶⁹⁾ have proposed the addition of supercalcine waste to cement to form a low temperature ceramic waste form. Samples consisting of commercial cement mixed with simulated radioactive waste were formed by either curing at 60°C or hot pressing at 150°C or 250°C at 50,000 psi (345 MPa). The amount of cesium leached hydrothermally in deionized water at 200°C compared to similar data for PNL 72-68 glass at 300°C; however, supercalcine by itself is less leachable. This is no surprise as supercalcine crystallizes into its assemblage of stable phases at temperatures between 900 to 1200°C. Hot pressed supercalcine has been produced at 900°C and 3000 psi. Thus, unless one incorporates into cement supercalcine which has been previously crystallized, it can not be expected to form a durable supercalcine product at temperatures as low as 60 to 250°C. Hot pressed supercalcine by itself has excellent impact strength and durability; thus, it would seem redundant to add it to cement.

Current studies at PNL involve the addition of 10% sintered supercalcine powder and untreated simulated waste calcine to Portland Type II cement. A simulated high sodium (PW-9) HLW is being used. Samples will be characterized as part of the PNL comparative study. Concrete samples containing calcine doped with curium-244 are being fabricated to study the effect of radiation on product inertness and radiolysis.

FIGURE 4. Leach Rates of Cs-137 from Grouts with Various Mix Additives

METAL MATRIX

Metal matrix encapsulation of nuclear wastes can serve 1) to increase thermal conductivity and lower internal temperatures, 2) to increase containment by increasing leach resistance and/or impact resistance.⁽⁸⁾ Utilization of a metal matrix produces a composite waste form which may contain either calcine, glass beads, or crystalline ceramic pellets. The ultimate multibarrier waste form would also provide a coating between the inner core and metal matrix.

Vacuum casting techniques have been developed at ICPP⁽⁸⁷⁾ and PNL.^(9,88) This technique is useful to achieve molten metal penetration into the inter-particle voids. Disc pelletized zirconia wastes and calcine have been encapsulated in lead and aluminum alloys. Four multibarrier concepts utilizing metal matrices, as outlined in Table 21, were demonstrated on a 1-liter scale by PNL. One of these concepts used a sintered metal matrix which may be either copper or stainless steels.

Direct casting of glass marbles in a lead matrix has been demonstrated by ANL on 2 in diameter by 2 ft high canisters.⁽⁸⁹⁾ In their studies they found that the voids were filled by the pressure of the lead melt above the canister. A zone cooling concept was used to eliminate casting voids.

TABLE 21. Multibarrier Waste Form Development One Liter Demonstration

<u>Inner Core</u>	<u>Coating</u>	<u>Matrix</u>	<u>Encapsulation</u>
72-68 Glass 10 mm Marble	None	Pb-10Sn	Vacuum Cast, 400°C
Supercalcine 7 mm	None	Al-12Si	Vacuum Cast, 650°C
Supercalcine 7 mm	Glass Glaze, <1 mm	Al-12Si	Vacuum Cast, 650°C
Supercalcine 2 mm	CVD PyC - 40 μ m Al ₂ O ₃ - 60 μ m	Cu	Gravity Sintered, 900° - 8 hr

Cermets, though not a metal matrix composite per se, are related and thus included for discussion. A cermet waste form has been developed at ORNL.^(134,146) This waste form consists of a continuous iron-nickel-base metal containing small particles of fission product oxides. The first stage of the process is to form calcined oxides from calcination of precipitated molten urea. The cermet is formed by hot pressing H_2 reduced calcine at 4000 psi and $100^\circ C$ or by extrusion followed by heat treatment at $1200^\circ C$ as illustrated in Figure 5.⁽⁹⁰⁾ Lab-scale (50 g) extruded and hot pressed samples containing simulated waste have been produced along with samples containing key radiotracers, such as Cs-137, Ru-106, and Sr-89. Cermets containing SRP sludge, SRP untreated acid, and NFS acid thorex wastes have been fabricated in hot cells and are being evaluated.⁽⁹¹⁾

Due to the composite nature of metal matrix and cermet waste form products, characterization is often difficult to perform and results are uncomparable. A summary of some property measurements on metal matrix waste forms is presented in Table 22.⁽⁹³⁾ It is interesting to note that leach resistance may not be greatly improved by a metal matrix. This is due to voids which may form between the inner core and the matrix. These voids create a continuous path for the solution to penetrate the inner waste form. It is possible to eliminate the voids by creating a slight reaction between the matrix and inner core. Inert coatings on the inner core may also be used. Coatings of pyrolytic carbon, PyC, and Al_2O_3 have shown considerable promise.^(10,92) (See Coatings Section).

Corrosion rates of metal alloys have been studied by Jardine et al.⁽⁹³⁾ and Braithwaite⁽⁹⁴⁾ under hydrothermal conditions. Jardine's studies were on candidate metal matrix materials. He observed a degradation of aluminum as shown in Table 23. Braithwaite was concerned with canister materials but his data is useful for metal matrix considerations. The effect of oxygenated water on increased leach rate was also observed (Tables 24 and 25). Van Geel observed a similar behavior for lead alloys in salt solutions.⁽⁹⁵⁾

Metal matrix and cermet development are continuing at ANL, PNL and ORNL. A full-scale demonstration of simulated waste glass marbles encapsulated in a lead alloy is planned at PNL. A scaled-up demonstration of uncoated super-calcine ceramic pellets in an aluminum alloy will follow utilizing the same

FIGURE 5. Laboratory Scale Operations Used to Produce Cermet Storage Forms from High-Level Waste

TABLE 22. Seven-Day Leach Rates in 25°C Distilled Stagnant Water for PW-7a Beads^(a) in Various Configurations in Lead Matrices

Isotope Analyzed	Fraction Leached per d			
	23 g Ingot ^(b)	7.5 g Ingot ^(c)	5.5 g Ingot ^(d)	Bare Beads ^(a)
⁶⁰ Co	8.4 x 10 ⁻⁶	2.5 x 10 ⁻⁵	2.0 x 10 ⁻⁵	5 x 10 ⁻⁵
⁶⁵ Zn	9.2 x 10 ⁻⁶	1.4 x 10 ⁻⁵	3.3 x 10 ⁻⁶	4 x 10 ⁻⁵
¹³⁴ Cs	2.1 x 10 ⁻²	1.1 x 10 ⁻²	2.9 x 10 ⁻²	3 x 10 ⁻²

(a) 85 wt% PW-7a calcine, 15 wt% glass frit disc pelletized-sintered beads.

(b) 54 beads in a 23 g ingot with 10.6 cm² exposed surface area.

(c) 17 beads in a 7 g ingot with 6.1 cm² exposed surface area.

(d) 13 beads in a 5 g ingot with 5.4 cm² exposed surface area.

TABLE 23. Results of 10-Day Autoclave Corrosion Test for Lead and Aluminum Alloy^(a)

Specimen	Capsule Atmosphere	Capsule Volume, cm ³	Initial wt, g	Final wt, g	Change in wt, g	Change in wt, %
<u>Lead</u>						
Pb 1	air	0.56	0.928 14	0.928 51	+0.000 37	+ 0.03
Pb 2	air	0.56	0.667 89	0.667 89	--	0
Pb 3	vacuum	0.56	0.701 55	0.701 31	-0.000 24	- 0.03
Pb 4	vacuum	0.56	0.123 37	0.124 59	+0.001 22	+ 0.99
<u>Aluminum^(b) Alloy</u>						
Al 1	air	0.24	0.083 16	0.079 21	-0.003 95	- 4.75
Al 2	air	0.24	0.081 76	0.078 20	-0.003 56	- 4.35
Al 3	N ₂	0.56	0.122 26	0.107 46	-0.014 80	-12.11
Al 4	N ₂	0.56	0.130 58	0.122 18	-0.008 48	- 6.49

(a) Test at 250°C and 5 MPa (750 psi) in saturated WIPPP salt.

(b) Al-12.5 wt% Si Alloy (ALCAN No. 46020).

TABLE 24. Corrosion Rates of Candidate Alloys In Deoxygenated Solutions^(a)

<u>Alloy</u>	<u>Brine A (mm/yr)</u>	<u>Brine B (mm/yr)</u>	<u>Seawater (mm/yr)</u>
1018 Mild Steel	1.7	0.07	0.4
Corten A Steel	0.9	0.05	0.2
2 1/4 Cr-1 Mo Steel	1.0 ^(c)	0.1 ^(c)	0.2
Lead	0.5	0.3	0.3
Copper	0.07	0.05	0.05
Naval Brass	1.0	-	1.0
90-10 Cupronickel	0.14	-	0.07
SS-304L	0.018	0.01	0.006
SS-316L	0.015	-	0.005
SS-Nitronic 50	0.008	-	0.003
SS-20Cb3	0.007	-	0.005
SS-Ebrite 26-1	0.016	-	0.005
Monel 400	0.03	-	0.1
Incoloy 825	0.006	-	0.004
Inconel 600	0.009	0.007	0.005
Inconel 625	0.005	0.001	0.012 ^(b)
Hastelloy C-276	0.07	-	0.0015
Zircaloy-2	0.001	-	-
Titanium C.P.	0.00	-	0.006
Ticode 12	0.006	-	0.005

(a) 250°C, P = 5MPa.

(b) Pitting corrosion.

(c) Crevice corrosion.

TABLE 25. Corrosion Rates of Candidate Alloys in Oxygenated Solutions^(a)

<u>Alloy</u>	<u>Brine A (mm/yr)</u>	<u>Seawater (mm/yr)</u>
1018 Mild Steel	7.0	11.0
Copper	1.2	5.0
Lead	1.2	1.0
90-10 cupronickel	0.4	0.7
SS-Ebrite 26-1	0.24	-
SS-20Cb3	0.1 ^(c)	-
Inconel 600	-	0.1
Hastelloy C-276	0.06 ^(b)	0.2 ^(b)
Ticode 12	0.004	-

(a) 250°C and P = 7MPa (O₂) = 600 ppm in Brine A and 1750 ppm in Seawater.

(b) Pitting and crevice corrosion.

(c) Crevice corrosion.

encapsulation equipment. Engineering feasibility and cost analysis are being conducted for metal matrix processes at both ANL and PNL.

Future efforts in the cermet program include continued process development and product characterization, especially in the areas of leach behavior, radiation stability, and phase identification. Engineering, safety, and economic evaluations are planned when sufficient process and product development has been performed.

REVIEW OF INTERNATIONAL WASTE FORM DEVELOPMENT

The present state of development of various waste forms in countries outside the U.S. is given in this section. The content is devoted to major efforts on waste form properties and characterization which have been reported in the literature. The section is organized in the same categories as the previous section: glass, sintered ceramics, glass-ceramics, hot-pressed ceramics, coatings, concrete, and metal matrix. Major activities by country will be found as sub-sections to the above categories. For reference, countries active in specific waste forms are indicated in Table 26.

GLASS

Canada (AECL)

The pioneering development of work on a bench-scale process for solidification of high-level-liquid waste glass in nepheline syenite glasses, $(\text{Na,K})_2\text{O}-\text{CaO}-\text{Al}_2\text{O}_3-\text{SiO}_2$, at the Chalk River Nuclear Laboratories (CRNL) was concluded in 1960.⁽⁹⁶⁾ Glass blocks were prepared by combining a mixture of 85% nepheline syenite and 15% lime with fission product solution in a ceramic crucible. The resulting gel was dried, denitrated at 900°C , and melted at 1350°C to form a glass. Volatile components, mainly ruthenium and cesium, were adsorbed on a heated bed of fire brick and iron oxides.

Two field tests were conducted. The first⁽⁹⁷⁾ consisted of 25 blocks containing ~ 300 Ci of aged fission products and made to a highly resistant formula, buried in a 5 x 5 block grid below the water table in the CRNL waste management area in August 1958. Twenty-five blocks containing ~ 1100 Ci of aged fission products were buried in a tighter 5 x 5 block grid at a similar location in May 1960.

From 1960 to 1967, the ^{90}Sr leaving the blocks has remained constant at a leaching rate of 5×10^{-11} g/cm²-d. The amount of glass being leached daily was calculated from the ^{90}Sr values for both the burial test results and laboratory test results as shown in Figure 6. For both cases the leach rate decreases with time. In 1963, 1966, and 1971, soil and water samples were

TABLE 26. International Waste Form Development

Country	Waste Form Type						
	Glass	Sintered Ceramic	Glass Ceramic	Hot-Pressed Ceramic	Coatings	Concrete	Metal Matrix
Australia (ANU)			X	X			
Austria (SGAE)					X		X
Belgium (Eurochemic)						X	X
Canada (AECL)	X						
England (AERE)	X						
France (Marcoule)	X						
Germany (HMI)			X				
Japan (PNC)		X	X				
Sweden (ASEA)				X

FIGURE 6. Canadian Waste Glass Leaching Experiment⁽⁹⁶⁾

taken from downstream of the blocks, and the plume of radioactivity that had left the blocks was delineated. The velocity of the ^{90}Sr front over a 12-year period was 2.75 m a^{-1} (7.53 mm/d).

Current Canadian specifications⁽⁹⁸⁾ for the reference package of high-level waste are shown in Table 27. The glass product is expected to incorporate a relatively small amount of fission product waste from either natural UO_2 or ThO_2 -based fuels. This dilute-waste composition was selected for two reasons: first, to keep the temperature increase in the waste and repository relatively low and, second, to minimize the number of different solidified waste types which may be produced at a fuel recycle facility. This will be done by combining the medium- and high-level waste streams.

The combination of high- and medium-level waste caused the glass formulation to be constrained by the concentration of sodium arising from the medium-level waste stream, and the fission product/sodium ratio of the combined waste stream. To maintain acceptable durability of the final high-level waste-glass product, it was essential to limit the Na_2O content to 20 wt%. This resulted in fission-product loading of <3 wt%. Borosilicate glasses were selected for development as matrices for the high- and medium-level waste. Three categories of borosilicate glass products were tested: waste- $\text{Na}_2\text{O-B}_2\text{O}_3\text{-SiO}_2$, waste- $\text{Na}_2\text{O-CaO-B}_2\text{O}_3\text{-SiO}_2$, and waste- $\text{Na}_2\text{O-ZnO-B}_2\text{O}_3\text{-SiO}_2$.

TABLE 27. Current Specifications for Canadian Reference Immobilized Waste Package

Container Dimensions	- diameter	0.46 m
	- length	3.03 m
Waste Glass	- volume	0.43 m^3
	- mass	1.08 Mg
	- fission product content	1 to 3 wt%
Decay Heat at 10 Years	- UO_2 fuel waste	0.2 kW/Mg
	- ThO_2 fuel waste	0.3 kW/Mg

The latter sodium borosilicate materials have been found in screening tests to be superior. Standard leach-rate tests at 100°C were used to compare the durabilities of these waste glasses. All initial work has been non-radioactive, and initial results are presented⁽⁹⁹⁾ in Table 28.

Because of the improved durability, the sodium zinc borosilicate glasses were selected for more detailed study of liquid-liquid phase separation behavior, of hydrothermal reaction, and alteration-zone product characterization. The addition of Na₂O to ZnO-B₂O₃-SiO₂ compositions suppresses the temperature at which phase separation occurs.

No crystalline products were recovered from hydrothermally-reacted Na₂O-B₂O₃-SiO₂ glasses after 10 days at 200°C. Studies on the alteration of large specimens of sodium borosilicate glasses confirmed that thick, silica-rich zones may develop which are depleted in Na and B. Hydrothermal alteration of powdered sodium zinc borosilicate glasses was studied at temperatures up to 200°C. Surface crystallization was readily detected after as little as four days exposure to water at 150°C. Glasses with a Zn:Si atom ratio of less than 1:2 yielded zincsilite, a zinc silicate which is structurally related to bentonite, as the major product.

Flow-through rock-glass leach test operated for more than a year at 22°C showed that species dissolved from a typical granite can significantly alter surface deposits formed on corroding glass. In a separate experiment, an identical glass sample was doped with ¹³⁷Cs. Leach rates were measured for over 600 days at 22°C for both the rock-glass sample and the control sample without granite. Leach rates were about 8.6×10^{-6} g/cm²-d in each case.

England (AERE)

Many glasses were examined^(100,101) in the UK for the immobilization of early wastes from materials testing reactors and defense wastes. These glasses include:

- CaO-SiO₂-B₂O₃
- Na₂O-SiO₂-B₂O₃
- Nepheline Syenite-CaO-B₂O₃

TABLE 28. Simulated High-Level Waste Canadian Glass Compositions and Range of Leach Rates Observed During 60-Day Test at 100°C

Product Number	Waste ^(a)	Product Composition/wt.%					IAEA Leach Rate (Na) at 5.2 Ms ₂ , 100°C μg/(m ² -s)	Comparative Leach Rates ^(b)
		Na ₂ O	ZnO	CaO	B ₂ O ₃	SiO ₂		
1	6.8	10.0	-	-	18.4	64.7	0.7	Na > (Al, Si)
2	10.1	15.0	-	-	16.6	58.2	2.3	Na > (Al, Si)
3	13.5	20.0	-	-	14.7	51.7	250.0	Na ~ Si > Al
4	16.9	25.0	-	-	12.9	45.2	140.0 ^(c)	Na > Si > Al
5	6.8	10.0	10.0	-	16.2	56.9	1.0	Na > Zn, (Si, Al)
6	10.1	15.0	10.0	-	14.4	50.5	1.5	Na > Zn, (Si, Al)
7	13.5	20.0	10.0	-	12.5	44.4	1.7	Na ~ Zn, (Si, Al)
8	16.9	25.0	10.0	-	10.7	37.4	-(d)	-
9	6.8	10.0	-	10.0	16.2	56.9	15.0	Na ~ Ca ~ Si ~ Al
10	10.1	15.0	-	10.0	14.4	50.5	26.0	Na ~ Ca ~ Si ~ Al
11	13.5	20.0	-	10.0	12.5	44.0	48.0	Na ~ Ca ~ Si ~ Al
12	16.9	25.0	-	10.0	10.7	37.4	-(d)	

(a) Composition of waste oxide mixture used in these experiments was (wt.%): FP oxides 17.2, ThO₂ 60.0, Al₂O₃ 16.0, AlF₃ 6.1, Fe₂O₃ 0.54, Cr₂O₃ 0.13, NiO 0.05.

(b) Concentrations of elements in brackets were below their detectable limit by AA.

(c) The sample was depleted in sodium at this point.

(d) These glasses were not leached for the full test period because of poor sample durability.

- $\text{Na}_3\text{PO}_4\text{-CaO-SiO}_2$
- $\text{Na}_3\text{PO}_4\text{-PbO-B}_2\text{O}_3$
- $\text{Na}_3\text{PO}_4\text{-SiO}_2$
- $\text{Na}_3\text{PO}_4\text{-Na}_2\text{SiO}_3$
- $\text{BPbO}_4\text{-Na}_2\text{O-SiO}_2$

All the phosphate glasses were found to be very corrosive to steel, and as they had no real advantages over borosilicate glasses were rejected during the 1960's.

These studies developed into the technological concept called Fingal, which involved the evaporation, denitration, and melting in a single process vessel which became the disposal vessel.⁽¹⁰²⁾ The concept included internal filters to reduce effluents, especially Ru losses. The "glasses" produced have the properties usually associated with glasses, but are very dark in color and contain separate crystalline material in dispersion in a glassy matrix.

The preferred glass compositions were of borosilicate glasses made at 1050°C. They were optimized for a waste composition which consisted of 45.8% of fission product mixed oxides, 20% Fe_2O_3 , 19% Al_2O_3 , 13% U_3O_8 , 1% MgO , 0.5% Cr_2O_3 , 0.4% NiO . Leach resistance was approximately the same in either distilled water or sea water at ambient temperatures. Storage temperatures were limited to 400°C to maintain low volatility.

In 1972, the UK vitrification program began again under the name of Harvest.⁽¹⁰³⁾ The Harvest program differed from FINGAL in that the scale was larger, the waste composition partly changed (see Table 29) and the internal filter was abandoned for conventional scrubbers.

The leachability of two glass compositions as described in Table 30 were studied in detail.⁽¹⁰⁴⁾ To determine the effect of possible waste stream variations and processing parameter changes, waste content was varied between 10 and 40 wt% and levels of MgO , Al_2O_3 , SO_4 , and PO_4 were varied from 1/2 to 2X normal. These variations did not affect the leach rates by more than 3 times that for the reference glass. High MgO glass had the worse leach rate.

TABLE 29. Comparison of FINGAL and Magnox Waste Compositions

	<u>FINGAL</u>	<u>Magnox Waste</u>
Al ₂ O ₃	19.2 wt%	20.0 wt%
MgO	0.8	24.8
Fe ₂ O ₃	20.0	10.6
U ₃ O ₈	13.3	0.2
NiO	0.4	1.4
Cr ₂ O ₃	0.5	2.2
FP0x	45.8	39.1
ZnO	--	1.7

TABLE 30. Composition of AERE Glasses(a)

<u>Number</u>	<u>SiO₂</u>	<u>B₂O₃</u>	<u>Na₂O</u>	<u>Li₂O</u>	<u>Waste</u>	<u>Formation Temperature</u>
189	41.5	21.9	7.7	3.7	25.3	950°C
209	50.9	11.1	8.3	4.0	25.7	1000°C

(a) Weight Percent Oxide.

Leach rates for glass 209 were lower than those for glass 189 by 5 to 10 times. Leach rates increased from 10^{-5} g/cm²-d at 25°C to 10^{-3} g/cm²-d at 100°C for glass 189 and from 10^{-6} to 10^{-4} for glass 209. Crystallization did not greatly affect the leach rates. Long-term leach rates of glass 189 containing ²³⁹PuO₂ were 1.5×10^{-6} g/cm²-d.

Johnson⁽¹⁰¹⁾ points out that the UK has, at various stages of development, methods for the conditioning of all gaseous, liquid, or solid wastes to solids. He states, "This can be done if society requires it, though not by extremes which go far beyond the safety of other human activities." Johnson also expresses the opinion "That ceramics are the obvious candidates and concludes the leach properties of these solids (Table 31) are generally sufficient to be comparable, in terms of environmental significance, to the more highly active, but more resistant, borosilicate glasses developed for Fingal and Harvest.

TABLE 31. Fixation Media for Nuclear Wastes

Waste	Isotope/Half-life	Form	Bulk Leachability ($\text{g/cm}^2\text{-day}$) ^(25°C) ^(h)
HAW	Various ($^{90}\text{Sr}/^{137}\text{Cs}$)	Glass	10^{-6}(a)
ZrO ₂ (+3% fuel)	Various (UO ₂ /PuO ₂ /FPs) ^(f)	Concrete/Glass	$3 \times 10^{-4}\text{(b)}$
MgO (+3% fuel)	Various (UO ₂ /PuO ₂ /FPs) ^(f)	Concrete/Glass	$3 \times 10^{-4}\text{(b)}$
Tritium	12y	PITC ^(d) /Polyacetylene/ZrH ₂	1.7×10^{-4} 1.8×10^{-8}
^{14}C	5736y	CaCO ₃ (concrete)	?
^{85}Kr	10.8y	Kr/Cu	$5 \times 10^{-4}\text{(c)}$
^{129}I	$1.6 \times 10^7\text{y}$	Solid solution	? ^(e)
^{22}Na	2.6y	Glass ^(g)	10^{-6}

(a) Extrapolated value.

(b) Polymer-impregnated cement is x 10 better.

(c) A worst value; control of water pH in the environment improves the figure, more refractory metal improves the figure and the cost.

(d) Polymer-impregnated tritiated concrete.

(e) Prediction over such long periods very difficult.

(f) ZrO₂ glass or cement will probably incorporate 3% UO₂ or PuO₂ by substitution solid solution. There should be less than 1%. Zirconium glasses tend to be rather high melting.

(g) Probably quite unnecessary.

(h) Data are for pure water at room temperature, and imply continued leaching by a replenished water flow.

France (Marcoule)

The French nuclear policy consists of reprocessing the irradiated fuels discharged from PWR's which are in operation, under construction and planned, and in reusing the separated plutonium in LMFBFR's⁽¹⁰⁵⁾ The transuranium solid wastes which will arise from PWR and LMFBFR reprocessing and fabrication plants--and among them the vitrified reprocessing first cycle raffinates--will be disposed of in geological formations. In order to improve the disposal safety, several processes have been developed in France. Vitrification was selected for immobilization of HLW. Development of ceramic (electromelt refractories and vitroceramics) containers as a second barrier is in progress.

France plans to utilize a multiple-barrier waste management system. The first barrier is the matrix in which the waste is embedded (e.g., glass). The second is the canister. The third is an artificial barrier, made with materials having good sorption properties for radionuclides. The fourth is the geological formation itself in which wastes will be deposited. Each barrier is considered independently and thus the policy is to make each barrier as efficient as possible independently of the others.

Development efforts have been concentrated on borosilicate glasses.⁽¹⁰⁶⁾ The first radioactive glasses were made in 1959. Acceptable leaching rates, the ease of the glass-making process, and flexibility to waste stream variations led to the definitive choice for vitrification.

This choice has led to several process demonstrations:

- The first glass blocks weighing 5 to 15 kg and having specific activities of about 1000 Ci/liter were made in 1963 by a gel technique in a graphite crucible. (Glasses stored since then have been retrieved after 15 yr for examination--no changes have occurred.)
- A pot vitrification technique has been developed in the Piver pilot plant at Marcoule. In 1969 to 1973, the Piver pilot plant, using this process, was operated under active conditions.

- Because of the successful operation of Piver, it was decided in 1972 to build an industrial vitrification plant at Marcoule. This plant started up in 1978 using a semi-continuous vitrification technique.^(107,108)
- A plant, using the continuous vitrification technique, will be capable of processing 500 m³/yr of waste solutions. The start up is scheduled for 1984-1985.

Sodium borosilicates and sodium aluminoborosilicate glasses have been selected as final materials in the field of the solidification of high-level radioactive wastes.⁽¹⁰⁶⁾ Examples of the glass compositions are given in Table 32. The main properties being investigated in relation to a long-term glass disposal are:

- The leach rate of the nuclides
- The effect of beta-irradiation
- The behavior of the materials under thermal conditions
- The effect of alpha-irradiation

The leach rates evaluated in a shielded cell from 2 kg glass blocks containing 100 to 1000 Ci of beta and gamma activity and leached by tap water at room temperature were found as 1 to 5 x 10⁻⁸ g/cm²-d based on Ru and Ce and 5 x 10⁻⁷ g/cm²-d based on Cs and Sr when the apparent steady state was reached. These values do not seem to be affected by the presence of a yellow phase in a high boron content glass (Table 33). Glass density ranged from 2.67 to 2.82 g/cm³. The maximum viscosity of the glass which is allowed with regard to the French vitrification process is 600 poise at 1100°C. This is easily met owing to the boron content of the various compositions. The volatilization of Ru, which may entail a blockage in the off-gas line due to a RuO₂ deposit, can be reduced by the use of sugar.⁽¹⁰⁹⁾

SINTERED CERAMIC

Japan (PNC)

O-Oka⁽¹¹⁰⁾ has developed sintered ceramic waste forms with compositions designed on mineralogical considerations. Candidate synthetic minerals such as nepheline, zirconia, aluminates, alumino-silicates, manganate, and titanate

TABLE 32. Example of Marcoule Glass Compositions

Reactor System	Weight Composition (%)							Volume Reduction Rate	Volume of Glass per ton of spent fuel
	SiO_2	Na_2O	B_2O_3	Al_2O_3	Fe_2O_3	Gd_2O_3	NiO + Cr_2O_3 F.P. and Actinides oxides		
LWR	47.6	12.4	18.6	--	6.4	--	low	5.5	94 l
FBR	46.0	15.0	17.9	6.3	3.6	5.2	0.3	4.9	205 l

TABLE 33. Leach Rate Values of Marcoule Glasses

		Leach Rate ($\text{g}/\text{cm}^2\text{-d}$)				
		B	Cs	Sr	Ru	Ce
20% B_2O_3 Glass	with Mo ^(a)	2×10^{-7}	2×10^{-7}	3×10^{-7}	9×10^{-7}	3×10^{-8}
	free of Mo	1.5×10^{-7}	3×10^{-7}	3×10^{-7}	1×10^{-7}	3×10^{-7}
14% B_2O_3 Glass	with Mo ^(a)	5×10^{-6}	2×10^{-5}	2×10^{-6}	1×10^{-7}	4×10^{-7}
	free of Mo	2×10^{-7}	7×10^{-7}	2×10^{-7}	1×10^{-7}	1×10^{-7}

(a) Presence of a yellow phase

ceramics were evaluated for the immobilization of simulated HLLW from the PNC reprocessing plant at Tokai, Japan. Compositions of candidate nepheline-type sintered ceramics and the required additives are listed in Table 34. For the nepheline-type sintered ceramics, waste loading is ~40 wt%.

TABLE 34. Compositions of Candidate PNC Nepheline Type Sintered Ceramics

Waste Oxides		Compounds	Additives (wt%)		
Constituents	(wt%)		Al_2O_3	SiO_2	SrO
Na_2O	33.8	$\text{Na}_2\text{O} \cdot \text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2$		56.14	65.54
ZrO_2	9.9	ZrO_2			
		$\text{ZrO}_2 \cdot \text{SiO}_2$		4.83*	
Cs_2O	5.1	$\text{Cs}_2\text{O} \cdot \text{Al}_2\text{O}_3 \cdot 4\text{SiO}_2$		1.85	4.35
Y_2O_3	1.3	$\text{Y}_2\text{O}_3 \cdot \text{Al}_2\text{O}_3$	0.59		
La_2O_3	3.0	$\text{La}_2\text{O}_3 \cdot \text{Al}_2\text{O}_3$	0.94		
Nd_2O_3	14.1	$\text{Nd}_2\text{O}_3 \cdot \text{Al}_2\text{O}_3$	4.27		
CeO_2	5.7	$\text{CeO}_2 \cdot \text{Al}_2\text{O}_3$	3.38		
NiO	1.9	$\text{NiO} \cdot \text{Al}_2\text{O}_3$	2.89		
Fe_2O_3	6.7	$\text{Fe}_2\text{O}_3 \cdot \text{Al}_2\text{O}_3$	4.36		
BaO	3.3	$\text{BaO} \cdot \text{MoO}_3$			
SrO	2.0	$\text{SrO} \cdot \text{MoO}_3$			
MoO_3	10.0	$\text{SrO} \cdot \text{MoO}_3 + \text{BaO} \cdot \text{MoO}_3$			2.2
Cr_2O_3	0.6	Dispersed			
Rb_2O	0.7				
Total	98.21		74.42	69.89	2.2
				(74.72)*	

Total of Additives

Composition A	146.51
Composition B	(151.34)*

* Numbers in parentheses indicate additive and totals for composition B.

Zirconia and manganate ceramics were formulated with additions of ZrO_2 or MnO_2 and SrO to the simulated waste. The content of the waste in the zirconia ceramics may rise to 60 wt%. Titanate ceramics were formulated with the addition of TiO_2 , SrO , Al_2O_3 , and in some cases SiO_2 .

Samples, 50 mm in diameter and 10 to 15 mm thick, of both types of sintered ceramic waste forms were produced by cold pressing and sintering at temperatures from 1000 to 1400°C. Additional samples were produced by hot pressing between 1200 to 1300°C at a pressure of 300 kg/cm² in an alumina mold. Dense nepheline sintered ceramics containing 30-40 wt% waste were obtained by sintering at 1300°C for 60-90 minutes and from hot pressing at 1250 to 1300°C for 30 minutes. Dense zirconate sintered ceramics were obtained for waste loadings from 40 to 50 wt% at similar processing parameters. Partial melting of both types of sintered ceramics was observed at 1400°C. Bulk densities ranging from 90 to 95% of theoretical (estimated) were obtained.

Crystalline phase content was determined by x-ray diffraction. In the nepheline-type composition, the main crystalline phase was identified as nepheline. Other crystalline phases including BaSrMoO_4 , NdAlO_3 , FeAlO_3 , and ZrSiO_4 were detected. Zircon and fluorite were detected in the zirconia-type ceramics along with several unidentified phases. Diffraction peaks observed in manganate and titanate ceramics were unidentified.

Leach resistance was measured by immersion in boiling water for 24 hr. Nepheline-type ceramics showed leach rates of 5×10^{-5} to 5×10^{-6} g/cm²-d. Zirconate ceramics had leach rates of 5×10^{-4} g/cm²-d and those of manganate and titanate-type were as high as 1×10^{-3} g/cm²-d.

Thermal expansion coefficients were also measured. Nepheline ceramics have coefficients of 90 to 105 $\times 10^{-7}/^\circ\text{C}$. Zirconia types have higher values of 130 to 160 $\times 10^{-7}/^\circ\text{C}$; manganate types have values of 110 to 150 $\times 10^{-7}/^\circ\text{C}$ and titanate types have values of 80 to 120 $\times 10^{-7}$. Thermal conductivities ranged from 0.01 to 0.05 W/cm-°K and bending strengths were in the range of 100 to 200 kg/cm².

GLASS CERAMIC

Germany (HMI)

Glass ceramics were developed at HMI as an alternative to glass waste forms.^(60,111) Spontaneous devitrification of waste containing glasses can be avoided by controlled crystallization after melting. Glass ceramics may offer improvements in waste form properties.

Four basic glass ceramic formulations were developed based upon the primary crystalline phases: celsian, diopside, eucryptite, and perovskite. Glass compositions are given in Table 35. All the glasses can be prepared at 1250°C and have viscosities of 100 poise at 1150°C. All glasses contained 20 wt% simulated-fission-product oxides. The glasses were converted to glass-ceramics by nucleation and heat treatment steps as described in Table 36 along with some other property information. Note that the celsian glass-ceramic does not require a nucleation step.

The resultant glass ceramics have improved impact resistance by an order of magnitude over that of glass samples. Leachability of the glass ceramics increased slightly but this was probably due to dissolution of the residual glass phase. All glass ceramics have a residual glass phase. In the case of waste containing glass-ceramics this phase can be as high as 50%. Often the residual glass phase has greater leachability than the original parent glass.

Further development has lead to glass ceramics with improved properties.⁽¹¹²⁾ One type, a fresnoite ($\text{Ba}_2\text{TiSi}_2\text{O}_8$) glass ceramic, has been developed, free of boron but still homogeneously digesting up to 15 wt% fission product oxides. The most outstanding features of this ceramic are its accommodation of Sr in a host phase (fresnoite) and the decreased leachability of the residual glass phase due to the lack of boron. Even more stable glass ceramics can be produced, e.g., a cordirite type, which requires melting temperatures of their parent glasses of up to 1400°C. This can be achieved if ceramic melters can be operated with ceramic electrodes.

Recent investigations have characterized both glasses and glass ceramics.^(113,114) One program, a joint effort of the European communities⁽¹¹⁵⁾ on characterization of waste forms is studying four borosilicate glasses and one

TABLE 35. Compositions of Parent Glasses and Crystal Phases of HMI Glass Ceramics

		Glass Ceramics					
		Celsian		Diopside		Eucryptite	Perovskite
Glass composition (wt%) (a)	SiO ₂	32-37		45-52		41-60	32-50
	Al ₂ O ₃	10-17		10-18		14-24	12-15
	B ₂ O ₃	5-8		1-5		4-11	5-10
	CaO	6-10		10-15		2-9	12-14
	BaO	18-23	MgO	5-10	BaO	0-5	
	Na ₂ O	2-6		0-10		0-3	5-8
	Li ₂ O	0-2		0-3		5-10	0-3
	TiO ₂	5-11		3-5	(+ZrO)	5-8	10-14
	ZnO	4-6		0-3		4-13	0-5
	Ca ₂ O	0-2	Fe ₂ O ₃	0-5			0-2
Crystal phases		H-celsian		diopside		β-eucryptite	perovskite
		(BaAl ₂ Si ₂ O ₈)		CaMg(SiO ₃) ₂		(LiAlSiO ₄)	CaMoO ₄ or
		perovskite (CaTiO ₃)		CaMoO ₄		CaMoO ₄	Mo-nosean
		BaMoO ₄		Mo-nosean		(Ce,Zr)O ₂	(Ce,Zr)O ₂
		pollucite		Na (AlSiO ₄ Na ₈)		Ca ₄ La ₆ (SiO ₄) ₆ (OH) ₂	pollucite
		(Cs,Na)AlSi ₂ O ₆		(AlSiO ₄) ₆ •MoO ₄		Li-Zn-silicates	
					pollucite		

(a) Excluding 20 wt% fission product oxides.

TABLE 36. Conditions for Preparation of HMI Glass Ceramics

<u>Properties</u>	<u>Celsian</u>	<u>Diopside</u>	<u>Eucryptite</u>	<u>Perovskite</u>
Melting temp. ($^{\circ}\text{K}$)	1470-1570	1470-1570	1370-1670	1520-1620
Transformation temp. ($^{\circ}\text{K}$)	830-860	880-930	740-830	860-890
Nucleation temp. ($^{\circ}\text{K}$) time (h)		925-970 5	800-850 3-5	900-940 3-5
Crystallization temp. ($^{\circ}\text{K}$) time (h)	1040-1130 6-15	1130-1230 10	900-1020 10-24	1070-1140 12-24
Leaching rates ($\text{g}/\text{cm}^2\text{-d}$) $\times 10^6$ glass ceramic	8-10 8-12	8-10 11-12	3-6 8-12	6-10 8-11
Thermal expansion $^{\circ}\text{C}^{-1} \times 10^7$	90-110	70-100	50-75	90-110

glass ceramic. Properties of these glasses are given in Table 37 (D-B1-3 is the glass ceramic). Leach rates of most of the products were unaffected⁽¹¹⁶⁾ by any heat treatment (i.e., crystallization).

Guber⁽¹¹⁴⁾ compared the properties of a borosilicate glass product (GP 98/12) and a glass ceramic product (VCP 15). The glass ceramic product had higher thermoconductivity and lower viscosity than the glass product. Some properties are summarized in Table 38. Soxhlet leach rates for the glass ceramic (VCP 15) were in the range of 10^{-5} to 10^{-6} g/cm²-d.

Japan (PNC)

Glass ceramic systems were studied by Oguino⁽¹¹⁷⁾ as candidates for immobilization of simulated HLLW from the reprocessing plant of PNC Japan. Four basic systems were evaluated: 1) CaO-MgO-Al₂O₃-SiO₂ (D system), 2) BaO-Al₂O₃-SiO₂ (C system), 3) CaO-TiO₂-Al₂O₃-SiO₂ (P system), 4) Li₂O-Al₂O₃-SiO₂ (E system). Compositions are listed in Table 39. The simulated oxides of HLLW of PNC Japan were contained by 20 to 30 wt% in the base glasses of these systems. The composition of simulated HLW oxides in wt% are: 30.6Na₂O, 9.05ZrO₂, 8.9MoO₃, 5.97Fe₂O₃, 4.61Cs₂O, 3.03BaO, 1.85SrO, 1.71NiO, 1.30MnO₂, 1.16TeO₂, 1.12Y₂O₃, 0.69Rb₂O, 0.57Cr₂O₃, 0.52CoO, 3.92La₂O₃, 5.11CeO₂, 2.31Pr₆O₁₁, 8.45Nd₂O₃, 1.02Sm₂O₃. Glasses were melted at 1300°C for 2 hr and cast into molds and annealed. The homogeneous glass obtained was crystallized by heating at a rate of 300°C/hr from room temperature to 500°C and subsequently heated at a rate of 33°C/hr from 500°C to maximum (crystallization) temperatures and held for 1 to 3 hr at these temperatures.

Crystal phases, as indicated in Table 39 were identified by x-ray diffraction. In the measurement of leach rate, samples of 25x25x5 mm were immersed in 500 ml of distilled water at 90°C for 24 hr, and weight loss and the amounts of Cs₂O and SrO dissolved into water were measured (Table 40). To evaluate the thermal stability, specimens were heated at 700°C for 1000 to 3000 hr and the change in crystal phases and leach rate were examined (Table 41). Other properties such as thermal expansion, thermal shock, and bending strength were determined for the glass ceramic system. Results for these parameters are given in Table 42.

TABLE 37. Properties of European Glass and Glass Ceramic Products

	<u>F-SON</u> <u>58.30.20</u>	<u>D-VG 98/3</u>	<u>UK-209</u>	<u>UK-189</u>	<u>D-B 1-3</u>
Glass preparation temperature $T_M, ^\circ K$	1425	1475	1275	1225	1475
100 dPas temperature $T_{100}, ^\circ K$	1475	1325	1490	1370	1365
Transformation temperature $T_g, ^\circ K$	823	793	773	773	823
Viscosity at 973K, dPas	3×10^8	5×10^5	1.6×10^6	5×10^5	$\sim 10^8$
Viscosity at 1073K, dPas	1.6×10^6	8×10^3	4×10^4	1×10^4	$\sim 3 \times 10^5$

TABLE 38. Properties of Glass and Glass Ceramics

	<u>Glass(a)</u> <u>(GP98/12)</u>	<u>Glass-Ceramic(b)</u> <u>(VCP 15)</u>
Density, g/cm ³	2.8	3.0
Viscosity at 1150°C, Pa · s	12.5	5.5
Thermoconductivity at 200°C, W/m-°K	1.2	2.2
Thermal Expansion, (K ⁻¹) x 10 ⁻⁶	N.D.	12.5
<hr/>		
(a) 15 wt% waste		
(b) 20 wt% waste		

As a conclusion of these evaluations, the diopside glass ceramic, D-62, was considered to be the most suitable for solidification of PNC HLLW. The diopside glass ceramic process was demonstrated by casting a monolith in a stainless steel canister with dimensions 3000 mm dia x 350 mm long x 5 mm thick. Properties of the resultant product are given in Table 43.

TABLE 39. Compositions and Crystal Phases of PNC Glass Ceramics

Composition wt%	Sample Number					
	D-62	C-27	P-50	E-63	D-210	P-71
SiO ₂	47.5	35.0	30.0	50.0	41.02	40.0
Al ₂ O ₃	6.8	15.0	10.0	12.5	8.20	6.5
B ₂ O ₃		5.0	5.0		3.50	3.5
Fe ₂ O ₃	9.5				8.70	
TiO ₂	2.7	5.0	10.0	6.0	3.20	10.0
CaO	6.8	4.0	25.0		4.10	10.0
MgO	6.8				1.37	
BaO		13.0				
ZnO		2.7		4.0		
Li ₂ O				7.5		
HLW	20.0	20.0	20.0	20.0	30.0	30.0
Total	100.0	100.0	100.0	100.0	100.0	100.0
Crystal	(a)	(b)	(c)	(d)	(a)	(e)
Phases	Fe ₃ O ₄ CaMoO ₄ CaTiO ₃	CaMoO ₄ CaTiO ₃	CaSiO ₃ CaMoO ₄ Sphene	Li ₂ SiO ₃	CaMoO ₄ Fe ₃ O ₄ CaTiO ₃	CaMoO ₄
Heat	1100°C	850°C	900°C	800°C	900°C	900°C
Treatment	1 hr	1 hr	3 hr	2 hr	1 hr	1 hr

- (a) Diopside (CaO•MgO•2SiO₂)
 (b) hexa-Celsian (BaO•Al₂O₃•2SiO₂)
 (c) Perovskite (CaTiO₃)
 (d) β-Spodumene (Li₂O•Al₂O₃•4SiO₂)
 (e) sphene (CaO•TiO₂•SiO₂)

HOT PRESSED CERAMICS

Australia (ANU)

A.E. Ringwood, of the Australian National University, has proposed two synthetic mineral waste forms, termed SYNROC, for the immobilization of HLW and defense wastes.^(118,119) The SYNROC concept utilizes low-waste loadings, usually about 10%. Because the radwaste ions are not major components (e.g., such

TABLE 40. Leach Rate of PNC Glass Ceramics(a)

Sample No.	Bulk Weight Loss	Leach Rate (g/cm ² -d)	
		Cs ₂ O	SrO
D-62	3.6 x 10 ⁻⁵	5.3 x 10 ⁻⁵	7.0 x 10 ⁻⁵
C-27	1.8 x 10 ⁻⁴	1.1 x 10 ⁻⁴	2.9 x 10 ⁻⁴
P-50	5.6 x 10 ⁻⁴	3.3 x 10 ⁻⁴	9.0 x 10 ⁻⁴
E-63	2.1 x 10 ⁻⁴	1.9 x 10 ⁻⁴	1.1 x 10 ⁻⁴
D-210	6.5 x 10 ⁻⁵	5.9 x 10 ⁻⁵	7.4 x 10 ⁻⁵
P-71	1.2 x 10 ⁻⁴	---	---

(a) Leach rate after immersion at 90°C for 24 hr in distilled water. Surface of 25 x 25 x 5 mm sample was polished by 1,000 mesh abrasive powder.

TABLE 41. Effect of Heat Treatment on Crystal Phases and Leach Rate of PNC Glass Ceramics(a)

Sample No.	Description of X-ray Trace	Leach Rate (Weight Loss, g/cm ² -d)		
		0 hr	1,000 hr	3,000 hr
D-62	No change	3.6 x 10 ⁻⁵	3.6 x 10 ⁻⁵	3.6 x 10 ⁻⁵
C-27	No change	1.8 x 10 ⁻⁴	1.9 x 10 ⁻⁴	---
P-50	Precipitate of NaAlSiO ₄ Appearance of Sphene (111) peak	5.6 x 10 ⁻⁴	8.5 x 10 ⁻⁴	1.6 x 10 ⁻³
E-63	Increase of intensity in Li ₂ SiO ₃ (110) peak	2.1 x 10 ⁻⁴	5.6 x 10 ⁻⁴	---
D-210	No change	6.5 x 10 ⁻⁴	6.5 x 10 ⁻⁵	6.6 x 10 ⁻⁵
P-71	No change	1.2 x 10 ⁻⁴	9.3 x 10 ⁻⁵	---

(a) After heating at 700°C for 1,000 3,000 hr

as supercalcine) but are distributed as dilute solid solutions, the host mineral phases provide the improved durability. Host mineral phases were selected which were known to be leach resistant in geologic environments.

The first synthetic waste form, SYNROC A, is comprised⁽¹²⁰⁾ of the phases perovskite (CaTiO₃), zirconolite (CaZrTi₂O₇), "Hollandite" (BaAl₂Ti₆O₁₆),

TABLE 42. Bending Strength, Thermal Expansion and Thermal Shock Resistance of PNC Glass Ceramics

Sample No.	Bending Strength (kg/cm ²)	Thermal Expansion	Transf.	Deform.	Thermal Shock Resistance
		$\alpha \times 10^7$ (1/°C) (30-380°C)	Pt. T _g (a) (°C)	Pt. T _f (b) (°C)	Temp. difference, ΔT (°C)
D-62	1320	79	794	>1000	150
C-27	760	91	545	838	120
P-50	870	81	582	>734	120
E-63	1270	78	502	734	150
D-210	1050	85	555	696	120
P-71	980	89	557	684	120

(a) T_g Dilatometric transformation point

(b) T_f Dilatometric deformation point

TABLE 43. Properties of D-62 Glass Ceramic Crystallized in Canister During Cooling

Crystal phases	Diopside, Fe ₃ O ₄ , CaTiO ₃ , CaMoO ₄
Leach rate wt. loss	4.3x10 ⁻⁵ g/cm ² -d
Cs ₂ O	5.6x10 ⁻⁵ g/cm ² -d
SiO ₂	7.5x10 ⁻⁵ g/cm ² -d
Bending strength	1100 kg/cm ²
Thermal expansion coeff.	81.8x10 ⁻⁷ /°C (30-380°C)
Softening temp.	>1100°C
Thermal conductivity	1.93 w/m-°C
Density	3.00 g/cm ³
Thermal stability	No change after heating at 700°C for 3,000 hrs.

Ba-felspar ($\text{BaAl}_2\text{Si}_2\text{O}_8$), kalsilite (KAlSiO_4), and leucite (KAlSi_2O_6) as defined in Table 44. This waste form was produced by melting at 1300°C and cooling to about 1150°C at $2^\circ\text{C}/\text{min}$. The melt crystallizes into the above specified mineral phases. This approach is similar to fusion melts and glass ceramic waste forms.

SYNROC A was found to be unaffected when exposed to pure water at 400°C and 1000 bars pressure for 24 hr.⁽¹²¹⁾ However, when subjected to identical conditions with a 10 wt% NaCl solution, the kalsilite and leucite phases were found to be unstable and cesium exchanged with sodium. Thus, a silicate-free synthetic-mineral-waste form was proposed to incorporate the cesium into the hollandite phase.

The composition of this silicate-free waste form, SYNROC B, is based upon three of the original phases ("hollandite", perovskite, and zirconolite). Distribution of radwaste elements under appropriate reducing conditions is summarized in Table 45. Because of the absence of silica, this waste form has a higher melting point than SYNROC A and is best prepared by solid-state sintering and/or hot pressing at about 1300°C . Since the silicates are absent from SYNROC B, the titania content is much higher and one may consider a similarity to the titanate ceramic developed by Sandia. However, the mineral and chemical composition are quite different.

The accelerated leach resistance of the SYNROC titanate ceramic was found by Ringwood to be excellent.⁽¹²²⁾ Electron probe microanalysis confirmed that Cs, Sr, and U were quantitatively retained by the three host phases after tests in saline solutions up to the extreme conditions of 900°C and 5000 bars. Also, no detectable change was found after 24 hr in disequilibrium conditions with SiO_2 -rich fluids at 800°C and 1000 bars.

For the immobilization of military or defense wastes, Ringwood proposes a ceramic material composed of the three normal SYNROC B phases plus large amounts of inert spinel and titanate phases which immobilize Al, Fe, and Mn. These latter phases include pseudobrookite (Al_2TiO_5 - Fe_2TiO_5 solid solution), ilmenite (FeTiO_3), ulvospinel (FeTi_2O_4), hercynite spinel (FeAl_2O_4), and a Ba-Al-Fe titanate ($\text{BaAl}_2\text{Fe}_2\text{Ti}_{13}\text{O}_{38}$). The waste form would preferably be

TABLE 44. Composition of SYNROC A and SYNROC B

	<u>SYNROC A</u>	<u>SYNROC B(a)</u>
Radwaste (wt.%)	10	10
Inert Additives (wt.%)	90	90
	<u>Composition of inert additives (wt.%)</u>	
SiO ₂	13	---
TiO ₂	33	60.4
ZrO ₂	10	9.9
Al ₂ O ₃	16	11.0
CaO	6	13.9
BaO	17	4.2
SrO	---	---
NiO	---	0.6
Na ₂ O	---	---
K ₂ O	5	---
Mineral Structures	"Hollandite", Perovskite Zirconolite, Ba-felspar, Kalsilite, Leucite.	"Hollandite," Perovskite, Zirconolite.

(a) "Hollandite" 35%, Zirconolite 31%, Perovskite 22%, plus additional TiO₂ (7%) and Al₂O₃ (5%) required for incorporation of radwaste components into SYNROC minerals.

TABLE 45. Summary of Distribution of Radwaste Elements Among SYNROC B Phases

<u>"Hollandite"</u>	<u>Zirconolite</u>	<u>Perovskite</u>
Mo ⁴⁺	<u>U</u> ⁴⁺	<u>U</u> ⁴⁺
Tc ⁴⁺	Th ⁴⁺	Th ⁴⁺
Cr ³⁺	<u>Pu</u> ⁴⁺	Cm ⁴⁺
Ni ²⁺	<u>Cm</u> ⁴⁺	Pu ⁴⁺
Fe ²⁺	<u>Am</u> ³⁺	Am ³⁺
K ⁺	<u>Y</u> ³⁺	Y ³⁺
<u>Cs</u> ⁺	REE ³⁺	REE ³⁺
Rb ⁺	<u>Na</u> ⁺	Sr ²⁺
Na ⁺		<u>Na</u> ⁺

formed by hot isostatic pressing in a metal container. A lower-density ceramic might be formed by cold pressing and sintering in a reducing atmosphere.

A few important process considerations should be noted. First, because of the dilute waste loading, the SYNROC B should be able to accommodate a wide variation in waste stream. Incorporation of the total radwaste stream into SYNROC has not been demonstrated. The development of SYNROC compositions was based upon the incorporation of 1 to 3 waste ions per synthesis. Sample quantities ranged from 100 to 200 mg. It has been recognized by Ringwood that the acceptance of waste stream variation would be severely limited at the proposed maximum waste loading of 30 wt%. Also modifications may be necessary for high Na waste streams.

The SYNROC additives need to be intimately and thoroughly mixed. It is preferable (possibly mandatory) that aqueous solution-suspensions be used to produce a starting material with high reactivity and homogeneity. Titanium is only available in soluble form as tetraisopropyl titanium $\text{Ti}(\text{O}i\text{C}_3\text{H}_7)_4$, although fine TiO_2 powders are available (e.g., pigment grade titania) which may be put into suspensions. Limited amounts (600 g) of SYNROC B containing 10 wt% Pw-4b type waste have been produced at PNL in a mini-spray calciner. Titania was successfully suspended in the liquid-feed solution by prior ballmilling for 24 hr.

Reducing conditions are essential for the successful immobilization of many radwaste species. For example, oxidizing conditions will produce Mo^{6+} , which prefers to crystallize into highly soluble alkali molybdate phases instead of the "hollandite" phase which incorporates the reduced species Mo^{4+} . Reducing conditions can be maintained by the addition of Ni powder (~ 0.6 wt%) and utilizing a Ni canister during hot pressing. Excess Al_2O_3 and TiO_2 are also required to ensure incorporation of Cs into the "hollandite" phase rather than less durable accessory phases.

The development of synthetic mineral waste forms is continuing at the Australian National University with primary emphasis on utilizing full level simulated nuclear waste and formulations for immobilization of defense wastes.

Sweden (ASEA)

Hot isostatic pressing, HIP, has been developed by ASEA to demonstrate the disposal of spent nuclear fuel by containment in alumina containers.⁽¹²³⁾ This process can be adapted to produce dense ceramic waste forms. Strontium titanate in a rutile matrix, cesium as pollucite in an aluminum-silicate matrix, and supercalcine have been processed into fully dense bodies.⁽¹²⁴⁾

The primary application of HIP as proposed by ASEA is to produce highly inert alumina canisters to contain either spent fuel or crystalline waste forms. Alumina canisters are produced by means of hot isostatic pressing in a QUINTUS press.^(a) The canister consists of a container and a lid. After the fuel rods or waste form have been placed inside the container, it is sealed by bonding together the container and lid. During this sealing operation by means of hot isostatic pressing, a completely tight, joint-free alumina canister is obtained. This can be subsequently deposited in deep geological formations, surrounded by a mixture of quartz sand and bentonite.

A large new QUINTUS press plant has been installed at ASEA's High-Pressure Laboratory in Robertsfors in the north of Sweden for the development of the method in full scale. The first of a series of full-scale alumina containers was recently (May 1978) made in the QUINTUS press by means of isostatic pressing.

The encapsulation process for spent fuel can be described as follows:

1. A container and a cover are produced by means of HIP from alumina powder. The container and cover are transferred to the encapsulation station.
2. The fuel rods are removed from their storage positions in the storage facility and transferred to the adjacent encapsulation station. The length of the fuel rods is reduced and then these are placed in a steel can.
3. The steel can with fuel rods is placed in the alumina container and the cover is fitted.

(a) ASEA

4. The alumina container and cover, surrounded by a thin metal jacket, are joined together by means of HIP to form a completely joint-free homogeneous body.
5. The sealed alumina canister is shipped to the final repository and stored there.

The same process could be used for crystalline waste forms except step 2 would be the production of a dense crystalline body by HIP of ceramic oxide powders. Several waste form options produced by HIP are proposed by ASEA as illustrated in Figure 7.

The properties of the HIP alumina are very good. The material is pressed to almost theoretical density. The density, 3.97 g/cm^3 , which corresponds to over 99.5% of the theoretical, is representative of the material hitherto produced. Alumina is a very hard material. A microhardness of 2100 H_V has been measured. For reference, high-speed steel normally has a hardness of 750 to 800 H_V . Thermal conductivity decreases from about $38 \text{ W/m}^\circ\text{C}$ at room temperature to about $7 \text{ W/m}^\circ\text{C}$ at 1500°C . Stainless steel has a heat transfer coefficient of $16 \text{ W/m}^\circ\text{C}$ at room temperature.

The bending strength lies between 450 and 500 MN/m^2 at room temperature, which corresponds to that of carbon steels. However, alumina at room temperature can only be deformed elastically and not also plastically like metals, thus its impact strength is limited. This is one disadvantage of alumina canisters. A metal jacket may be required to protect from impact during transport.

Test specimens taken from the joint zone have a bending strength equal to that of the parent material. Thus, the seal is excellent and there is no strength degradation in this area. Residual tensile stresses in the outer surface of the alumina canister were determined. Measurements show that residual tensile stresses can be maintained at a satisfactorily low level, if a suitably arranged sealing cycle is used.

FIGURE 7. Ceramic Encapsulation of Nuclear Waste Using ASEA's High-Pressure Technology

COATINGS

Austria (SGAE)

Pyrocarbon, PyC, and nickel coatings have been applied to simulated waste granules by chemical vapor deposition at SGAE by Neumann.^(125,126) The granules were obtained from the output of the fluidized-bed calcine of the Eurochemic pilot plant.⁽¹²⁷⁾ The phosphate granules ranged from 0.7 to 2.0 mm mean diameter.

Conventional CVD PyC coatings are applied using C_2H_2 and Ar at temperatures above $1000^{\circ}C$.⁽¹²⁸⁾ At these temperatures the phosphate granules tended to stick together. The use of a catalyzer, nickel tetracarbonyl, was used to lower the coating temperature to $525^{\circ}C$.

Pure nickel coatings were also applied by CVD using nickel tetracarbonyl.⁽¹²⁹⁾ Temperatures of only $200^{\circ}C$ are required in this process. The nickel provides an inert barrier coating around the porous granules and also prevents intergranular point contact during encapsulation. Leaching media often has access to encapsulated particles by the continuous path created by porous particle contact.

Characterization of the coated particles showed that pores and cracks in the particles were well sealed by either the PyC or NI coatings. Average nickel layer was $45\text{ }\mu\text{m}$ and PyC layer, $100\text{ }\mu\text{m}$. Soxhlet leach tests on Ni and PyC coated particles resulted in no detectable weight loss. Neumann's studies are very significant in that PyC was applied at $525^{\circ}C$ and this process would be compatible with the coating of glass marbles.

CONCRETE

Belgium (Eurochemic)

Eurochemic has developed a process to encapsulate structural material, cut from the fuel elements, into a polymer concrete matrix.⁽¹³⁰⁾ The matrix material is a mixture of an inorganic aggregate (SiO_2 , kaolin), a polymer as a binder, and chemical additives such as fire retardants $Al(OH)_3$ and water repellent

chemicals (e.g., paraffins). Special efforts are made to keep the weight fraction of the polymer low ($\leq 20\%$) in order to yield a product with low content of organic material.

A matrix material composed of 50 wt% SiO_2 , 10% kaolin, 20% $\text{Al}(\text{OH})_3$, and 20% of a polyester based on orthophthalic acid, styrene, and glycol was used. The incorporation can be performed under water to reduce airborne contamination problems. Water is, however, an inhibitor for most polymerization reactions. The aggregate material was, therefore, pretreated with water repellent paraffins, prior to mixing the aggregate with the polymerizable compounds.⁽¹³¹⁾

Demonstration products containing 50% contaminated solids with a radiation dose of 100 R/hr at contact were fabricated. The matrix material was found to have excellent flame and fire resistance (ASTM oxygene index 30), no porosity, high resistance to thermal shocks, a compression strength of 140 MPa, and no visual change after an accumulated radiation dose of 10^{10} rad.

METAL MATRIX

Austria (SGAE)

Neuman^(132,133) has investigated three methods for encapsulation of simulated waste calcines: vacuum pressure casting, centrifugal casting, and stirring. Tests were primarily conducted on an Al-12%Si alloy because of its excellent casting properties. Tests with a Pb-2%Sb-1%Sn alloy were limited to vacuum-pressure casting. Simulated waste calcine granules from the fluidized-bed calcine of Eurochemic pilot plant were used. The granules were held in a stainless steel basket during casting. A gap was provided between the cage and canister wall to provide for a zone free of waste granules.

Centrifugal casting provides a driving force to fill the voids by canister rotation. In this process a crucible containing molten metal was placed next to one containing waste granules. The crucibles are rotated and the metal was forced into the granule container. The intergranular void gas was simultaneously pushed out. The process resulted in an excellent void-free product but has considerable scale-up difficulties and maintainance requirements.

In the stirred or "thixo" casting process, simulated waste granules and fines were heated by induction with the Al-Si alloy. At a few degrees above the melting point a mechanical stirrer mixed the components to incorporate the fines into the granule-metal mixture to form a highly viscous metal melt. The container was then rapidly cooled. The results were promising since fines could be encapsulated but the product contained porosity and would produce a contaminated stirrer. No property data was reported.

Belgium (Eurochemic)

Metal matrices were considered⁽¹³⁰⁾ by Eurochemic to improve the long-term stability of waste products through improved thermal conductivity (lower internal temperatures) and increased corrosion resistance (metal barrier). Early studies demonstrated that leach rates 1×10^{-6} g/cm²-d were possible. These studies⁽¹³⁵⁾ utilized mineral-type phosphate granules (MINERVA Process) encapsulated in lead alloys and were called "Ceramets."⁽¹³⁶⁾ The primary process developed at Eurochemic produces small glass beads which are encapsulated into molten alloys of aluminum and lead. This waste form, termed "Vitromet," has been demonstrated both on an industrial scale and in a hot-cell.⁽¹³⁷⁾ The technique developed at Eurochemic has also been applied to the granular phosphate product from the LOTES process.⁽¹³⁸⁾

The encapsulation process is dependent upon the properties of both the matrix and the material to be encapsulated. Glass beads can be directly poured into canisters containing molten aluminum alloys. If the metal matrix has a density higher than the glass or ceramic beads, then alternate processes must be developed.

Eurochemic developed a process to encapsulate glass beads into lead which incorporates a double-walled stainless steel container, as illustrated in Figure 8. The inner compartment is first filled with glass beads by an inlet tube which is subsequently sealed. The outer container is heated by induction heating to about 500°C. Lead shot is fed between the inner and outer wall. The molted metal rises up by an opening in the bottom of the inner container. The container is zone cooled from the bottom to the top to eliminate casting voids.

The corrosion behavior of various lead and aluminum alloys is being studied by Eurochemic. Results for the corrosion of lead alloys in salt solutions

FIGURE 8. Embedding of Glass Beads into a Lead Matrix

are described in Table 46. The corrosion increase in air-saturated salt solutions is proposed to be due to cathodic processes created by O_2 . Pure aluminum appears to be as equally corrosion resistant as lead in certain chloride-containing solutions. Delta- and eta-alumina and $Al_{11}(OH)_{30}Cl_3$ passivation layers were found to form on the surface of alluminum alloys in contact with salt.

Reactions between the stainless steel canister wall and either lead or aluminum alloys were not observed after the encapsulation process (~ 7 hr). A slight reaction was observed between phosphate glass beads and pure lead. A slight enrichment of Na and Al in the glass phase extended $10\text{ }\mu\text{m}$ in from the metal interface and lead diffused into the glass phase $\sim 40\text{ }\mu\text{m}$.

Thermal conductivity of $\geq 10\text{ W/m-}^\circ\text{C}$ is reported for vitromets. This is an order of magnitude greater than typical glass blocks ($\sim 1\text{ W/m-}^\circ\text{C}$). Impact strength was estimated by measuring the compressive strength of vitromets. For 3-5 mm phosphate beads in Pb-Sb (2 wt%) alloy, compression had to be continued to 5-15% before rupture occurred.

The technology to produce vitromet waste forms was applied in the PAMELA process⁽¹³⁹⁾ to demonstrate immobilization of HLLW on a 1/3 scale. Glass beads were produced at a rate of 6 kg/hr (2 T LWR fuel per day) by passing liquid glass through platinum nozzles onto a rotating steel disc. The glass drops solidify to form glass beads and are swept off the disc by a compressed air stream. The beads were encapsulated with Pb-Sb into a vitromet product 22 cm in diameter and 1 m in height.

A lab-scale PAMELA plant was constructed and installed in two hot cells at Julich from 1973 to 1974. Approximately 15 kg of phosphate glass beads were produced. The glass beads were encapsulated at Eurochemic in Mol. Two blocks were produced: 8 cm diameter by 10 cm high and 14 cm diameter by 10 cm high. Contamination of the outside canister and of the hot cell was negligibly low. A full-scale demonstration plant is planned.

TABLE 46. Corrosion Rate of Lead Alloys in Dry ASSE Salt and Aqueous Solutions Saturated with the ASSE Salt(a)

Corrosion Condition	Temp. (°C)	Corrosion Period (days)	Corrosion rate (mm yr ⁻¹)					
			Pb99.99	Pb99.9Cu	Pb-Sb	Pb98.5	Pb-Sn20	Pb-Sn10
Dry ASSE II salt ^(b)	110	151-176	0.0008	0.0004	0.0004	0.0007	0.0001	
Immersion in saturated solution of ASSE salt								
a) Saturated with pure N ₂ and under N ₂ atmosphere	50	106	0.0004	---	---	0.0009	---	0.004
b) Saturated with air	50	92	---	---	---	0.016	---	0.013

(a) Determined according DIN 50905

(b) Composition (wt%) Cl (50); Na (39); SO₄ (1.2); Ca₄ (0.4); Fe (6x10⁻⁴); Mg (<0.1)

COMPARISON OF WASTE FORM PROPERTIES

Several glass and alternative waste forms are currently being developed at U.S. and foreign laboratories. These waste forms include glass, sintered ceramics, concrete, glass ceramics, hot-pressed ceramics, metal matrices, and coated pellets. Although many of the waste forms are in their initial stages of development, a summary of existing property characteristics is given in Table 47.^(a) In general, proposed alternative waste forms have properties falling within a relatively narrow range.

An important topic of discussion is the comparison of crystalline and amorphous waste forms. Current consensus^(6,7,92) is that either glass or crystalline materials can be shown to have some advantage when a single property is considered. For example, the volatility of crystalline waste forms is generally less than that of glasses. The impact resistance of crystalline ceramics is greater than that of glass. Glass waste forms offer advantages in ease of processing and radiation stability. Crystalline processes often require complex operations and many process steps such as hot pressing, disc pelletization, chemical vapor deposition, and sintering. Concrete may offer less complex processes if pressing is not required.

CHEMICAL DURABILITY

Chemical durability is of importance as the primary mechanism for release of radioactivity from waste solids, which involves water leaching and then groundwater transport to the biosphere. A comparison of leach rates of potential waste forms and other materials in both high-temperature (250°C) brine and moderate-temperature (99°C) distilled water is shown in Table 48. These results are based on weight loss and indicate the relative behavior of materials. Note that the maximum difference is a factor of 50. The comparisons indicate that, while differences between materials exist, those differences are relatively small.

(a) There are many products listed in Table 47 whose property data are not complete. A comparative testing program is being conducted at PNL to provide a more complete property assessment.

TABLE 47. Properties of Alternative Waste Forms

Waste Form	Bulk Soxhlet Leachability g/cm ² -d	Volatility wt% at 800°C	Impact Resistance	Bulk Density, g/cm ³	Porosity, %	Thermal Conductivity, W/m-°K	Waste Loading, wt%
Sintered Supercalcine	10 ⁻⁵ to 10 ⁻⁶	-0.05 in 72 hr	N/A	2.2 to 4.2	10 to 40	N/A	65 to 80
Hot Pressed Supercalcine	N/A	-0.01 in 72 hr	4.5 wt% <37 μm at 158 ft-lb	4.0 to 4.9	N/A	0.8 to 1.5	65 to 80
Sintered Ceramic	10 ⁻⁴ to 10 ⁻⁵	N/A	N/A	2.5 to 3.2	8 to 25	0.17	30 to 80
Sintered Titanate	10 ⁻⁴ to 10 ⁻⁵	+0.34 in 475 hr	N/A	4.1 to 4.3	1	2.76	22 to 25
Glass Ceramic	10 ⁻⁴ to 10 ⁻⁶	N/A	5.0 wt% <1 mm at 44 ft-lb	~3	None	1.5	20
Hot Pressed Concrete	slight wt gain	N/A	N/A	N/A	N/A	N/A	14 to 20
Concrete	~10 ⁴	N/A	+20-30 cm ² J	7	N/A	0.3 to 2.0	10 to 50
Glass Marbles in Pb-10Sn Cast Matrix	N/A	N/A	0.1 wt% <37 μm at 158 ft-lb	6.3	N/A	7.3 to 9.0	21
Coated Super- calcine in Cu Gravity Sintered Matrix	N/A	N/A	1 wt% <37 μm at 158 ft-lb	3.5	N/A	12 to 24	34
Cermet	10 ⁻⁵ to 10 ⁻⁷	No loss	N/A	6.2 to 7.4	N/A	20 to 200	20 to 75
Waste Glass	10 ⁻⁴ to 10 ⁻⁶	-0.10 in 72 hr	9 wt% <37 μm at 158 ft-lb	3.0 to 3.4	None	0.8	30 to 50

(a) N/A = not available

TABLE 48. A Leach Rate Comparison of Materials⁽¹³⁹⁾

<u>Material</u>	<u>99°C Distilled Water, g/cm²-d</u>	<u>250°C Salt Brine, g/cm²-d</u>
Al ₂ O ₃	1 x 10 ⁻⁶	2 x 10 ⁻⁴
Supercalcine	8 x 10 ⁻⁶	1 x 10 ⁻⁴
Waste Glass	9 x 10 ⁻⁶	7 x 10 ⁻⁴
Granite	1 x 10 ⁻⁵	6 x 10 ⁻⁴
Soda-Lime Glass	5 x 10 ⁻⁵	3 x 10 ⁻³

Chemical durability at hydrothermal conditions has been determined for both crystalline and glass waste forms. Data from PNL^(139,140) and Pennsylvania State University^(139,141) on concentrations of fission product ions in solution after testing are shown in Table 49. Braithwaite⁽⁵⁹⁾ has found similar results for glass, supercalcine, and sintered titanates, as shown in Table 50. The percent altered indicates the extent of reaction zone at the leached surface.

In addition to the hydrothermal testing of simulated waste glass and supercalcine, PSU has also determined the hydrothermal "reactivity" of spent fuel and coated ceramic waste forms. The results⁽¹¹⁾ of several hundred tests are summarized in Table 51. Note the extreme stability of the coated ceramic (PyC/Al₂O₃) pellets in 400°C brine. It is important to note that the differences in solution concentration between glass and supercalcine are not large. Glass is lower in some cases and supercalcine in others. This implies that differences in "thermodynamic stability" are not very important from a solubility point of view.

VOLATILITY

Volatility is of importance primarily during waste form processing as radionuclides may be released if high temperatures are required. Volatility data is necessary to conduct risk analyses on potential accident conditions, such as fire, during processing or transport.

TABLE 49. Concentration of Fission Products Leached from Glass and Supercalcine Materials⁽¹³⁹⁾

Elements ^(c)	PNL (a) (WIPP Brine)		Penn State(a) (USGS N8T-6a Brine)		Penn State(a) (Distilled water)		PNL (a) (Distilled water)		PNL (a) (Basalt)	PNL Long-Term Static Test ^(b)
	Glass (76-68)	Super- calcine (SPC-4)	Glass (76-68)	Super- calcine (SPC-4)	Glass (76-68)	Super- calcine (SPC-4)	Glass (76-68)	Super- calcine (SPC-4)	Glass (76-68)	Glass (76-68)
	7 days	3 days	28 days	28 days	28 days	28 days	21 days	21 days	21 days	3 years
Cs	650	2210	500	1600	49	22	37	20	0.3	1.30
Rb	67	487	64	470	10	41	24	11	0.15	-
Sr	12	53	160	1300	0.64	1.4	1.3	4.3	0.31	1.04
Ba	-	-	-	-	0.5	6.9	-	-	-	-
Mo	830	40	45	22	1110	540	940	34	1.6	-

(a) Autoclave tests at 350°C

(b) Room-temperature tests

(c) ppm in solution

TABLE 50. Matrix Alteration and Cs Solubility After Leaching Copper Borosilicate Glass, Supercalcine, and Titanate Ceramic

Leachant	Copper Borosilicate Glass		Supercalcine		Titanate Ceramic	
	% Altered	% Solubilized Cs	% Altered	% Solubilized Cs	% Altered	% Solubilized Cs
D. I. Water	75	12	12	4	10	4
NaCl Brine	13	1	17	14	2	5
Mg ⁺² Brine	50	5	4	7	2	4
Seawater	49	8	6	1	ND	ND

(a) At 250°C, 17.9 MPa, and 90 days

TABLE 51. Reactivity of Waste Forms in Various Environments

	Hydrothermal Reactivity			Salt Brine Alteration of Solid
	Alteration of Solid	"Silicate Groundwaters"	Waste-Rock Interaction Effects	
Spent Fuel (200°C)	Uranite (UO ₂) Unaltered	Major <u>Cs</u> , Rb, Mo Trace <u>U</u>	Cs, Rb, Mo "Fixed" UO ₂ stable in low Eh solutions	Not studied
Reference Glass (300°C)	Complete	Major Na, B, Mo, Cr Minor <u>Cs</u> , Si, Ni, Rb, Ca Trace <u>U</u> , <u>Ln</u> , <u>Sr</u> , Ba	Most elements in solution fixed by interactions New mineral-like phases	Not crystallized
Current Crystalline Ceramic (300°C)	None(a)	Minor Na, Rb, Mo, Si Trace <u>Cs</u> , <u>Sr</u> , Ba, Ca	Any released elements fixed Solid-solid interactions minor or absent	Several minerals altered Others stable
Coated Ceramic (400°C)	None	None	None	None

(a) Crystallinity of synthetic minerals enhanced, NCS phase crystallized.

Gross weight loss for glass (72-68) and supercalcine (SPC-2 and SPC-4) simulated waste forms is given in Figure 9.⁽⁹²⁾ Results for cesium are summarized in Figure 10 for several PNL glasses, for a Purex-type calcine composition (PW-4b), and for several hot-pressed supercalcine formulations.⁽⁶⁾ Also, some single-point data are shown for $\text{CsAlSi}_2\text{O}_6$ and CsAlSiO_4 . It is important to recognize that the fractional losses shown reflect the surface area size and the time period used in the experiments. In a comparative sense, the results clearly show crystalline forms have volatility losses 10 to 100 times lower than typical waste glasses. For glasses, the presence of water has a small effect, and addition of alumina reduces cesium volatility, probably by simple increase of the viscosity. It is of note that unconsolidated calcine PW-4b shows high losses at 800°C.

IMPACT

During transport and handling of the waste form package, accident situations may occur which will deliver high impact energy to the package. Impact resistance of waste forms has been determined at PNL on a lab-scale by dropping weights onto the sample positioned in an enclosed die and measuring particle size distribution by sieve analysis.⁽³⁸⁾ The fine particles <10 μm size are of most concern as they represent the respirable fraction.

The surface area of impacted samples is plotted in Figure 11. Although the total surface area of supercalcine cores is much greater than that of waste glass or soda-lime marbles, the actual increase in surface area with impact is less. The surface area for supercalcine cores, waste glass marbles, and soda-lime glass marbles increases upon impact at 158.4 ft-lb by a factor of 4, 556, and 521, respectively. The impact results for soda-lime marbles, waste glass marbles, and waste glass right-circular cylinders do not significantly differ on a surface area/g basis.

Since the supercalcine cores contained considerable porosity, additional impact tests were conducted on hot-pressed supercalcine, which represents a product of optimum density.⁽¹⁰⁾ To determine the best possible impact resistance of a ceramic product, tests were also conducted on a sample of

FIGURE 9. Gross Weight Loss of Waste Forms after 4 hr in Dry Air

FIGURE 10. Cesium Loss from Waste Materials in Four Hours at Various Temperatures

FIGURE 11. Surface Area of Supercalcine and Other Waste Forms After Impact Tests at Various Forces

FIGURE 12. Particle Size Distribution of Waste Forms After Impact of 158.4 ft-lbs

Al₂O₃ grinding media. The results for both samples after impact at 158.4 ft-lb are compared with the previous waste glass cylinder in Figure 12. The dense supercalcine resulted in a factor of 2 reduction in production of fines <37 μm as compared to glass. The impact resistance of the Al₂O₃ grinding media illustrates that a factor of 5 reduction in fines <37 μm could possibly be obtained with use of ceramic products instead of glass.

RADIATION STABILITY

It is well recognized that the intense radiation fields within solidified nuclear wastes cause measurable property changes. All materials under serious consideration, including glasses, glass-ceramics, supercalcines, and cements have been or are being studied. Waste glasses have been the most thoroughly studied, with specific reports available concerning stored energy,⁽¹⁴²⁾ helium diffusion,⁽¹⁴³⁾ and more general discussions.^(18,37,38)

Although experiments are in progress to evaluate gamma field and transmutation effects (Cs → Ba) on both glasses and crystalline waste forms, the major interest has been in evaluating damage from alpha-decay of the actinide elements, which is the major source of atomic displacement in solid wastes.⁽¹⁴²⁾ Most of the experimental work involves use of ²⁴⁴Cm or ²³⁸Pu as dopants to accelerate dose rates by factors of 10³ to 10⁵. Radiation effects in glasses have been simulated to >10⁵ years for commercial HLW and to >10⁶ years for lower-activity defense wastes. The work on supercalcines and on glass-ceramics has been undertaken to simulate times of ~10³ years.

Density or volumetric changes are of importance since excessive or mismatched (i.e., a waste form may contain components which change in different directions or rates) changes may create cracks and loss of product integrity. Bibler and Kelley⁽²¹⁾ measured a positive dilation due to internal alpha radiolysis of borosilicate glasses containing ²⁴⁴Cm or ²³⁸Pu, as shown in Figure 13. The simulated waste had an effect upon this dilation as indicated by a smaller increase for glass containing Pu only.

The work of Ross et al.⁽⁶⁾ is summarized in Figure 14. Figure 14A summarizes the volumetric changes determined by density measurement for a variety

FIGURE 13. Positive Dilatation Due to Internal Alpha Radiolysis of Borosilicate Glasses Containing ^{244}Cm or ^{238}Pu

of waste glasses (number coded), supercalcine, and a glass-ceramic. In Figure 14B, results obtained by x-ray diffraction for several actinide compounds are given, either from PNL studies or from the literature. The density changes for waste solids are small and can be negative for some glasses. An individual crystalline material, even when contained within a waste form as for (1) RE apatite^(a) in supercalcine, or (2) RE titanite^(a) in glass ceramics, can have much larger changes, which will introduce stress into the solid.

Measurements of stored energy, impact strength, helium diffusivity, and leach rate have been made on waste glasses, and they show minor radiation induced changes that do not significantly alter the initial properties. Phase stability has been determined for supercalcine under alpha exposure.⁽¹⁰⁾ The apatite phase is found to disappear after an equivalent alpha-exposure of 200 years, as shown in Figure 15. Although leaching of radiation-damaged supercalcine was not studied, recent work on a devitrified glass by Weber et al.⁽¹⁴⁴⁾ suggests that amorphization of apatite may not significantly affect leach rates.

BULK PROPERTIES

Bulk properties of waste forms are important in processing considerations. Parameters, such as internal temperature, canister requirements, heat content, and material requirements may be determined from the bulk properties and waste form composition.

(a) Numbers correspond to designations in Figure 14.

FIGURE 14. Effect of Radiation on the Density of (A) Waste Solids and (B) Crystalline Phases

FIGURE 15. Ratios of Integrated Intensities (apatite/fluorite and tetragonal/fluorite)

CONCLUSIONS

There are numerous alternative waste form concepts available both in the U.S. and in foreign countries for the immobilization of high level nuclear wastes. The development level of these concepts varies from full-level radioactive demonstrations for cast glass to lab-scale nonradioactive demonstration of new concepts such as SYNROC and FUETAP. Since glass has had several years of development as a waste form, many of the alternatives to glass need additional research and development to bring their state of development up to that of glass.

Waste form property information is at a stage to allow one to determine trends but more data is required to make a complete and thorough comparison. The data presented in the previous section supports one current view that the properties of alternative waste forms, as presently developed, fall within a narrow range and no single waste form offers optimum properties in all areas of concern; exceptions to this are coated particles. Recent results with PyC and Al_2O_3 coated samples show that these waste forms may totally prevent leaching for hundreds of years. Many alternatives have shown considerable promise such as the synthetic mineral concept of SYNROC, the multibarrier approach with coated particles in a metal matrix, and the high-pressure-high-temperature ceramics.

In the final decision on waste form selection one must consider the total waste management system. Canister design, overpacks, engineered barriers and absorbents, and the geologic repository must be considered. This concept has been presented by Mendel⁽¹⁸⁾ for glass cast in canisters as illustrated in Figure 16. Another concept utilizes an interdependent system of sequential barriers as the core of the radioactive waste management strategy.^(11,145) The inner core consists of pellets of nearly theoretically dense ceramics (prepared by modern sintering or hot pressing methods) composed of several phases each modelled on high resistant mineral phases. The pellets would be coated with a layer of PyC and/or Al_2O_3 . These pellets would be embedded in a lead matrix, and sheathed in an outer layer of 1-2 cm of pure lead. Alternatively, the pellets could be hot pressed in a ceramic matrix with an outer skin of 1-2 cm.

FIGURE 16. Protective Barriers for HLW During Geologic Disposal

In conclusion, several waste form options and multiple barrier waste management systems are potentially available when one considers all of the possible combinations. The properties of these systems must be determined by comparative tests and the process feasibility must be established by scaled-up demonstrations to ensure that waste management technologies are available at an appropriate date.

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REFERENCES

1. Technology for Commercial Radioactive Waste Management, DOE-ET-0028 (May 1979).
2. H. C. Shefelbine, Evaluation of the Characteristics of Defense Transuranic Wastes, SAND-78-1850, Sandia Laboratory (November 1978).
3. Alternative Processes for Managing Existing Commercial High Level Radioactive Wastes, NUREG-0043 (April 1976).
4. J. C. Hall, Conceptual Liquid Waste Storage and Solidification Baseline Description, NMS-7, Savannah River Laboratory (September 1977).
5. G. K. Oertel, "The DOE Program in High Level Waste Immobilization," Proceedings of High Level Radioactive Solid Waste Forms, Denver, NUREG/CP-0005, National Technical Service, Springfield, VA (1979).
6. W. Lutze, "Glassy and Crystalline High Level Nuclear Waste Forms: An Attempt of Critical Evaluation," Proceedings of Ceramics in Nuclear Waste Management, Cincinnati, CONF-790420, Technical Information Center, Oak Ridge, TN (1979).
7. W. A. Ross, J. E. Mendel, R. P. Turcotte, and J. M. Rusin, "A Comparison of Glass and Crystalline Waste Materials," Proceeding of Ceramics in Nuclear Waste Management, Cincinnati, CONF-790420, Technical Information Center, Oak Ridge, TN (1979).
8. L. J. Jardine and M. J. Steindler, A Review of Metal-Matrix Encapsulation of Solidified Radioactive High Level Waste, ANL-78-19, Argonne National Laboratory (May 1978).
9. J. M. Rusin, R. O. Lokken, J. M. Lukacs, K. R. Sump, M. F. Browning, and G. J. McCarthy, Multibarrier Waste Forms Part I: Development, PNL-2668-1, Pacific Northwest Laboratory (1978).
10. J. M. Rusin, J. W. Wald, and W. J. Gray, Multibarrier Waste Forms Part II: Characterization and Evaluation, PNL-2668-2, Pacific Northwest Laboratory (1979).
11. R. Roy, "Step-Function Increase of Significance of Waste Form in RWM Strategy," Proceedings of Symposium on Waste Management, Tucson (February 1979).
12. W. A. Ross, J. M. Rusin, and J. L. McElroy, "Processes for Production of Alternative Waste Forms," Proceedings of Symposium on Waste Management, Tucson (February 1979).

13. L. L. Hench, "Alternative Forms for the Storage of Nuclear Waste," Testimony given to Hearings on Nuclear Waste Management, Subcommittee on Energy Research and Production, U.S. House of Representatives Committee of Science and Technology, May 15-17, 1979, Washington, D.C.
14. J. L. McElroy and W. A. Ross, "Alternative Solidified Forms for Nuclear Waste," ANS Proceedings of the First Pacific Basin Conference on Nuclear Power Development and the Fuel Cycle (October 1976).
15. Alternatives for Managing Wastes from Reactor and Post-Fission Operations in the LWR Fuel Cycle, Vol. 2, p. 6.64, ERDA-76-43 (May 1976).
16. J. E. Mendel, "High-Level Waste Glass," Nuclear Technology, 32, 72 (1977).
17. J. E. Mendel, W. A. Ross, R. P. Turcotte, and J. L. McElroy, "Physical Properties of Waste Glass," Proceedings of High Level Radioactive Solid Waste Forms, Denver, NUREG/CP-0005, National Technical Information Service, Springfield, VA (1979).
18. J. E. Mendel, The Storage and Disposal of Radioactive Waste as Glass in Canisters, PNL-2764, Pacific Northwest Laboratory (December 1978).
19. M. J. Kupfer, W. W. Schultz, C. W. Hobbick, and J. E. Mendel, Glass Forms for Alpha Waste Management, ARH-SA-239, Atlantic Richfield Hanford Company (July 1975).
20. J. A. Ledford and P. M. Williams, "Utilization of Borosilicate Glass for Transuranic Waste Immobilization," Proceedings of Ceramics in Nuclear Waste Management, Cincinnati, CONF-790420, Technical Information Center, Oak Ridge (1979).
21. N. E. Bibler and J. A. Kelley, Effect of Internal Alpha Radiation on Borosilicate Glass Containing Savannah River Plant Waste, DP-1482, Savannah River Laboratory, Aiken, SC (May 1978).
22. J. A. Kelley, Evaluation of Glass as a Matrix for Solidification of Savannah River Plant Wastes--Radioactive Studies, DP-1397, Savannah River Laboratory (October 1975).
23. J. A. Kelley, Evaluation of Glass as a Matrix for Solidification of Savannah River Plant Waste--Nonradioactive and Tracer Studies, DP-1382, Savannah River Laboratory (May 1975).
24. R. M. Wallace, H. L. Hall, and R. F. Bradley, Solid Forms for Savannah River Plant High Level Waste, DP-1335, Savannah River Laboratory (December 1973).
25. M. J. Kupfer and W. W. Schulz, Fixation of Hanford Sludge by Conversion to Glass, ARH-SA-285, Atlantic Richfield Hanford Company (March 1977).

26. M. J. Kupfer, Fixation of Hanford Alkaline Waste Liquors by Conversion to Glass, RHO-SA-20, Rockwell Hanford Operations (April 1978).
27. M. J. Kupfer, Vitrification of Hanford Bismuth Phosphate and Uranium Recover Process Sludges, RHO-LD-60, Rockwell Hanford Operations (September 1978).
28. Integrated Radioactive Defense Waste Management Plan, Vol. 1, Program Management Plan, SRO-TWM-78-1, Savannah River Office (August 1978).
29. Report of the Panel on Waste Solidification, NUREG/CR-0895, National Academy of Sciences, Washington, D.C. (July 1979).
30. Techniques for the Solidification of High Level Wastes, Technical Report Series No. 176, International Atomic Energy Agency, Vienna (1977).
31. D. W. Clelland and A. D. W. Corbett, "The Management of High Level Liquid Wastes from Reprocessing Operations," Proceedings of Nuclex 78, 5th International Fair and Technical Meetings of Nuclear Industries, Switzerland (October 3-7, 1978).
32. K. J. Schneider, "Solidification and Disposal of High Level Radioactive Wastes in the United States," Reactor Tech. 13, 387 (1970-1971).
33. J. M. White and G. LaHaie, Ultimate Fission Product Disposal, the Disposal of Curie Quantities of Fission Products in Siliceous Materials, CRCE-591, Atomic Energy of Canada Ltd. (1955).
34. L. C. Watson, R. C. Durham, W. E. Erlebach, and H. K. Rae, "The Disposal of Fission Products in Glass," Proceedings of 2nd UN International Conference Peaceful Uses Atomic Energy, 1958, Geneva, 18, 27, United Nations, NY (1958).
35. M. I. Goldman, J. A. Servizi, R. S. Daniels, T. H. Y. Tebbutt, R. T. Burns, and R. A. Lauderdal, "Retention of Fission Products in Ceramic-Glaze-Type Fusions," Proceedings of 2nd UN International Conference Peaceful Uses Atomic Energy, 1958, Geneva, 18, 27, United Nations, NY (1958).
36. J. L. McElroy, K. J. Schneider, J. N. Hartley, J. E. Mendel, G. L. Richardson, R. W. McKee, and A. G. Blasewitz, Waste Solidification Program Summary Report, Vol. 11, Evaluation of WSEP High Level Waste Solidification Processes, BNWL-1667, Pacific Northwest Laboratory (July 1972).
37. J. E. Mendel, W. A. Ross, F. P. Roberts, Y. B. Katayama, J. H. Westsik, Jr., R. P. Turcotte, J. W. Wald, and D. J. Bradley, Annual Report on the Characteristics of High Level Waste Glasses, BNWL-2252, Pacific Northwest Laboratory (June 1977).

38. W. A. Ross et al., Annual Report on the Characterization of High Level Waste Glasses, PNL-2625, Pacific Northwest Laboratory (June 1978).
39. G. J. McCarthy, S. Komarneni, B. E. Scheetz, and W. B. White, "Hydrothermal Reactivity of Simulated Waste Forms and Water Catalyzed Waste Rock Interactions," Proceedings of Scientific Basis for Nuclear Waste Management, Boston, Plenum, NY (1979).
40. D. Gombert II, H. S. Cole, and J. R. Berreth, Vitrification of High Level ICPP Calcined Wastes, DOE Report ICP-1177, Allied Chemical Corporation (February 1979).
41. J. R. Berreth, D. Gombert II, and H. S. Cole, "Vitrification of ICPP High Level Zirconia Calcine," Proceedings of Ceramics in Nuclear Waste Management, Cincinnati, CONF-790420, Technical Information Center, Oak Ridge (1979).
42. M. J. Kupfer, "Vitrification of Hanford Radioactive Wastes," Proceedings of Ceramics in Nuclear Waste Management, Cincinnati, CONF-790420, Technical Information Center, Oak Ridge (1979).
43. M. J. Plodinec, "Development of Glass Compositions for Immobilization of Savannah River Plant Waste," Proceedings of Scientific Basis for Nuclear Waste Management, Boston, Plenum, NY (1979).
44. M. J. Plodinec and J. R. Wiley, "Viscosity and Electrical Conductivity of Glass Melts as a Function of Waste Composition," Proceedings of Ceramics in Nuclear Waste Management, Cincinnati, CONF-790420, Technical Information Center, Oak Ridge (1979).
45. J. R. Wiley, Electrical Resistivities of Glass Melts Containing Simulated SRP Waste Sludges, DOE Report DP-1488, Savannah River Laboratory (1978).
46. J. R. Wiley and J. H. LeRoy, "Long-Term Leach Rates of Glasses Containing Actual Waste," Proceedings of Ceramics in Nuclear Waste Management, Cincinnati, CONF-790420, Technical Information Center, Oak Ridge (1979).
47. W. N. Rankin and J. A. Kelley, "Microstructure and Leachability of Vitrified Radioactive Wastes," Nucl. Tech., 41, 373 (December 1978).
48. D. M. Strachan, Crystalline Materials for the Long-Term Storage of Hanford Nuclear Defense Waste, RH0-SA-13, Rockwell Hanford Operations (May 1978).
49. K. M. Lamb, Final Report: Development of a Metal Matrix for Incorporating High-Level Commercial Waste, ICP-1144, Allied Chemical Corporation (March 1978).
50. K. M. Lamb and H. S. Cole, Development of a Pelletized Waste Form for High-Level ICPP Zirconia Wastes, ICP-1185, Allied Chemical Corporation (April 1979).

51. W. A. Ross, "Sintering of Radioactive Wastes into a Glass Matrix," (Abstract), Bull. Am. Ceramic Soc., 54 (1975).
52. J. M. Rusin, Applicability of Alternative Waste Forms for Immobilization of Alternative Fuel Cycle Wastes, PNL-2775, Pacific Northwest Laboratory (1979).
53. D. M. Strachan and W. W. Schulz, "Characterization of Pollucite as a Material for the Long-Term Storage of Cesium-137," ARH-SA-294, submitted to J. Amer. Ceram. Soc. (June 1977).
54. J. K. Johnstone and B. T. Kenna, "Fixation of Radiocesium in Ceramics for Beneficial Applications," (Abstract), Bull. Am. Ceram. Soc., 56(3), 342 (1977).
55. C. W. Christenson et al., "Radioactive Waste Disposal, Pt. III," Ceramic Age, 31 (August 1964).
56. R. L. Schwoebel and J. K. Johnstone, "The Sandia Solidification Process-- A Brief Overview," ERDA Workshop Ceramic and Glass Radioactive Waste Forms, D. W. Ready and C. R. Cooley (eds), CONF-770102 (April 1977).
57. B. T. Kenna, K. D. Murphy, and H. S. Levine, "Long-Term Elevated Temperature Leaching of Solid Waste Forms," Scientific Basis for Nuclear Waste Management, Plenum, NY (1979).
58. J. K. Johnstone, T. J. Headley, D. F. Hlava, and F. V. Stohl, "Characterization of a Titanate Based Ceramic for High Level Nuclear Waste Solidification," Scientific Basis for Nuclear Waste Management, Plenum, NY (1979).
59. J. W. Braithwaite and J. K. Johnstone, "Chemical Durability and Characterization of Nuclear Forms in a Hydrothermal Environment," Proceedings of Symposium Ceramics in Nuclear Waste Management, CONF-790420, Cincinnati, April 30-May 2, 1979, Technical Information Center, Oak Ridge, TN (1979).
60. A. D. De et al., "Development of Glass Ceramics for the Incorporation of Fission Products," Bull. Am. Ceram. Soc., Vol. 55(5), 500 (May 1976).
61. G. H. Beall and H. L. Rittler, "Basalt Glass Ceramics," Bull. Am. Ceram. Soc., 55(6), 579 (1976).
62. G. H. Beall and H. L. Rittler, "Process for Forming a Basaltic Glass Ceramic Product," U.S. Patent 3,557,575 (1971).
63. G. J. McCarthy and M. T. Davidson, "Ceramic Nuclear Waste Forms: Part II. A Ceramic-Waste Composition Prepared by Hot Pressing," Bull. Am. Ceram. Soc., 55 190, (1976).

64. J. G. Moore, E. Newman, and G. C. Rogers, Radioactive Waste Fixation in FUETAP (Formed Under Elevated Temperature and Pressure) Concretes-- Experimental Program and Initial Results, ORNL/TM 6573, Oak Ridge National Laboratory (March 1979).
65. D. M. Roy and G. G. Gouda, "High-Level Radioactive Waste Incorporation Into Special Cement," Nucl. Tech., 40, 214 (1978).
66. J. G. Moore, G. C. Rogers, J. H. Paehler, and H. E. Devaney, "FUETAP (Formed Under Elevated Temperatures and Pressures) Concretes as Hosts for Radioactive Wastes," Proceedings of Ceramics in Nuclear Waste Management, Cincinnati, CONF-790420, Technical Information Center, Oak Ridge (1979).
67. D. M. Roy and G. R. Gouda, Hot Pressed Cement in Radioactive Waste Management, Final Report to Nuclear Waste Technology Program, Sub-contract 841, Pacific Northwest Laboratory (August 1974).
68. D. M. Roy, "Cement Based Nuclear Waste Solidification Forms," Proceedings of High-Level Radioactive Solid Waste Forms, Denver, NUREG/CP-0005, National Technical Information Service, Springfield, VA (1979).
69. D. J. Roy, M. W. Grutzeck, A. K. Sarkas, and S. D. Atkinson, "A Low Temperature Ceramic Radioactive Waste Form, Proceedings of Ceramics in Nuclear Waste Management, Cincinnati, CONF-790420, Technical Information Center, Oak Ridge (1979).
70. J. A. Stone, Evaluation of Concrete as a Matrix for Solidification of Savannah River Plant Waste, DP-1448, Savannah River Laboratory (June 1977).
71. Quarterly Progress Report, Research and Development Activities, Waste Fixation Program, October-December 1973, BNWL-1809, Pacific Northwest Laboratory (January 1974).
72. J. L. McElroy, compiler, Quarterly Progress Report, Research and Development Activities, Waste Fixation Program, April-June 1974. BNWL-1841, Battelle, Pacific Northwest Laboratory, Richland, WA, p. 63-68 (July 1974).
73. J. L. McElroy, compiler, Quarterly Progress Report, Research and Development Activities, Waste Fixation Program, July-September 1974. BNWL-1871, Battelle, Pacific Northwest Laboratory, Richland, WA, p. 46 (November 1974).
74. J. L. McElroy, compiler, Quarterly Progress Report, Research and Development Activities, Waste Fixation Program, January-March 1974. BNWL-1826, Battelle, Pacific Northwest Laboratory, Richland, WA, p. 41-43 (April 1974).

75. A. M. Platt, compiler, Quarterly Progress Report, Research and Development Activities, Waste Fixation Program, October-December 1973. BNWL-1809, Battelle, Pacific Northwest Laboratory, Richland, WA, p. 55-60 (January 1974).
76. J. L. McElroy, compiler, Quarterly Progress Report, Research and Development Activities, Waste Fixation Program, April-June 1975. BNWL-1932, Battelle, Pacific Northwest Laboratory, Richland, WA, p. 57 (September 1975).
77. J. L. McElroy, compiler, Quarterly Progress Report, Research and Development Activities, Waste Fixation Program, July-September 1975. BNWL-1949, Battelle, Pacific Northwest Laboratory, Richland, WA, p. 47 (January 1976).
78. J. L. McElroy, compiler, Quarterly Progress Report, Research and Development Activities, Waste Fixation Program, January-March 1976. BNWL-2070, Battelle, Pacific Northwest Laboratory, Richland, WA, p. 31-32 (1976).
79. McCarthy, G. J., "Crystalline and Coated High Level Waste Forms," Proceedings of the Conference on High Level Radioactive Solid Waste Forms, U.S. Nuclear Regulatory Commission, Denver, Colorado (December, 1978).
80. Alternatives for Long-Term Management of Defense High-level Radioactive Waste, ERDA 77-42/1 (1977).
81. R. O. Lokken, A Review of Radioactive Waste Immobilization in Concrete, PNL-2654, Pacific Northwest Laboratory (June 1978).
82. D. Columbo and R. M. Neilson, Jr., "Some Techniques for the Solidification of Radioactive Wastes in Concrete," Nucl. Tech., 32(1), 30 (1977).
83. A. J. Stone, "Studies of Concrete as a Host for Savannah River Plant Radioactive Waste," Proceedings of Scientific Basis for Nuclear Waste Management, Boston, Plenum NY (1979).
84. H. O. Weerer, J. G. Moore, and E. W. McDaniel, "Waste Disposal by Shale Fracturing at ORNL," Proceedings of Scientific Basis for Nuclear Waste Management, Boston, Plenum, NY (1979).
85. J. G. Moore, H. W. Godbee, and A. H. Kibbey, "Leach Behavior of Hydrofracture Grout Incorporating Radioactive Wastes," Nucl. Tech., 32(1), 39 (1977).
86. R. Blanco, "Comment on Cement Based Nuclear Waste Solidification Forms," Proceedings of High-Level Radioactive Solid Waste Form, NUREG/CP-0005, Denver, December 12-21, 1978, NTIS, Springfield, VA (1979).

87. K. M. Lam, Final Report: Development of a Metal Matrix for Incorporating High-Level Commercial Waste, ICP-1144, Allied Chemical Corporation (March 1978).
88. J. M. Rusin, M. F. Browning, and G. J. McCarthy, "Development of Multibarrier Nuclear Waste Forms," Proceedings of Scientific Basis for Nuclear Waste Management, Boston, Plenum, NY (1979).
89. L. J. Jardine and M. J. Steindler, "A Perspective of Metal Encapsulation of Waste," Proceedings of Scientific Basis for Nuclear Waste Management, Boston, Plenum, NY (1979).
90. W. S. Aaron, T. C. Quinby, and E. H. Kobisk, "Cermet High Level Waste Forms," Proceedings of Scientific Basis for Nuclear Waste Management, Boston, Plenum, NY (1979).
91. W. S. Aaron, T. C. Quinby, and E. H. Kobisk, "Development of Cermets for High Level Radioactive Waste Fixation," Proceedings of Ceramics in Nuclear Waste Management, Cincinnati, April 30-May 2, 1979, Technical Information Center, Oak Ridge, TN (1979).
92. J. M. Rusin, R. O. Lokken, and J. W. Wald, "Characterization and Evaluation of Multibarrier Nuclear Waste Forms," Proceedings of Ceramics in Nuclear Waste Management, Cincinnati, April 30-May 2, 1979, Technical Information Center, Oak Ridge, TN (1979).
93. L. T. Jardine et al., "Metal Matrix Encapsulation of High Level Wastes" Fuel Cycle Programs Quarterly Report, ANL-78-37, Argonne National Laboratory, Argonne, IL (October-December 1977).
94. J. W. Braithwaite and M. A. Molecke, "High-Level Waste Canister Corrosion Studies Pertinent to Geologic Isolation," Proceedings of Scientific Basis for Nuclear Waste Management, Boston, Plenum, NY (1979).
95. J. Van Geel et al., "Incorporation of Solid High Level Wastes into Metal and Non-Metal Matrices," Proceedings of High-Level Radioactive Solid Waste Forms, NUREG/CP-0005, Denver, December 19-21, 1978, National Technical Information Service, Springfield, VA (1979).
96. W. F. Merritt, "High-Level Waste Glass: Field Leach Test," Nucl. Tech., 32, 88 (1977).
97. A. R. Bancroft and J. D. Gamble, Initiation of a Field Burial Test of the Disposal of Fission Products Incorporated into Glass, AECL-718, Atomic Energy of Canada Ltd. (1958).
98. D. J. Cameron and G. G. Strathdee, "Materials Aspects of Nuclear Waste Disposal in Canada," Proceedings of Ceramics in Nuclear Waste Management, Cincinnati, CONF-790420, Technical Information Center, Oak Ridge (1979).

99. G. G. Strathdee, N. S. McIntyre, and P. Taylor, "Development of Alumino-Silicate and Borosilicate Glasses as Matrices for CANDU High-Level Waste," Proceedings of Ceramics in Nuclear Waste Management, Cincinnati, CONF-____, Technical Information Center, Oak Ridge, TN (1979).
100. J. R. Grover and B. E. Chidley, Glasses Suitable for the Long-Term Storage of Fission Products, AERE R3178 (1960).
101. K. D. B. Johnson, J. R. Grover, and W. H. Hardwick, "Work in the UK on Fixation of Highly Radioactive Wastes in Glass," Third Geneva Conference on Peaceful Uses of Atomic Energy, p. 188, (1965).
102. K. D. B. Johnson, "The UK Program--Glasses and Ceramics for Immobilization of Radioactive Wastes for Disposal," Proceedings of Ceramics in Nuclear Waste Management, Cincinnati, CONF-790420, Technical Information Center, Oak Ridge (1979).
103. J. B. Morris and B. E. Chidley, "Preliminary Experience with the New Harwell Inactive Vitrification Pilot Plant," in Management of Radioactive Wastes from the Nuclear Fuel Cycle, International Atomic Energy Agency, Vienna (1976).
104. K. A. Boulton, J. T. Dalton, A. R. Hall, A. Hough, and J. A. C. Marples, "The Leaching of Radioactive Waste Storage Glasses," Proceedings of Ceramics in Nuclear Waste Management, Cincinnati, CONF-790420, Technical Information Center, Oak Ridge (1979).
105. Y. Sousselier, "Use of Glasses and Ceramics in the French Waste Program," Proceedings of Ceramics in Nuclear Waste Management, Cincinnati, CONF-790420, Technical Information Center, Oak Ridge (1979).
106. R. A. Bonniaud, N. R. J. Francillon, F. L. Lande, and C. G. Sombret, "Glasses as Materials Used in France for the Management of High-Level Wastes," Proceedings of Ceramics in Nuclear Waste Management, Cincinnati, CONF-790420, Technical Information Center, Oak Ridge (1979).
107. R. Bonniaud, A. Jouan, and C. Sombret, "Large-Scale Waste Glass Production," Proceedings of High-Level Radioactive Solid Waste Forms, Denver, NUREG/CP-0005, National Technical Information Service, Springfield, VA (1979).
108. R. Bonniaud and C. Sombret, "State of the Research in the Field of Solidification of High-Level Radioactive Wastes in France," 77th Annual Meeting of the American Ceramic Society, Washington, D.C. (May 1975).
109. R. Bonniaud, A. Jouan, and C. Sombret, "Status of the French AVM Vitrification Facility" Waste Management 79, Proceedings, Tucson (February 1979).

110. K. O-Oka, T. Ohta, S. Masuda, and N. Tsunoda, "Solidification of HLLW into Sintered Ceramics," in Proceedings of the Conference on Ceramics in Nuclear Waste Management, Cincinnati, CONF-790420, Technical Information Center, Oak Ridge, TN (1979).
111. A. K. De et al., "Fixation of Fission Products in Glass Ceramics," IAEA-SM-207111, International Symposium on the Management of Radioactive Wastes from the Nuclear Fuel Cycle, Vienna (March 22-26, 1976).
112. W. Lutze, "Glass and Glass-Ceramic Waste Form Characterization," Proceedings of Scientific Basis for Nuclear Waste Management, Boston, Plenum, NY (1979).
113. G. Malow, "An Investigation of Crystallization in Glasses Containing Fission Products," Proceedings of Ceramics in Nuclear Waste Management, Cincinnati, CONF-790420, Technical Information Center, Oak Ridge, TN (1979).
114. W. Guber, M. Hussain, L. Kahl, W. Muller, and J. Saidl, "Development and Characterization of the Glass Ceramics VCP-15 for Immobilization of High-Level Liquid Radioactive Waste," Proceedings of Ceramics in Nuclear Waste Management, Cincinnati, CONF-790420, Technical Information Center, Oak Ridge, TN (1979).
115. G. Malow, V. Beran, W. Lutze, J. A. C. Marples, J. T. Dalton, A. R. Hall, A. Hough, and K. A. Boulton, Testing and Evaluation of the Properties of Various Potential Materials for Immobilizing High Activity Waste, First Annual Report EUR 6213 EN, Commission of the European Communities (1978).
116. K. A. Boulton, J. T. Dalton, A. R. Hall, A. Hough, and J. A. C. Marples, "Leaching of Radioactive Waste Storage Glasses," Proceedings of Ceramics in Nuclear Waste Management, Cincinnati, CONF-790420, Technical Information Center, Oak Ridge, TN (1979).
117. N. Oguino et al., "Solidification of HLLW by Glass-Ceramic Process," in Proceedings of the Conference on Ceramics in Nuclear Waste Management, Cincinnati, CONF-790420, Technical Information Center, Oak Ridge, TN (1979).
118. A. E. Ringwood, Safe Disposal of High-Level Nuclear Reactor Wastes: A New Strategy, Australian National University Press, Canberra (1978).
119. A. E. Ringwood, S. E. Kesson, N. G. Ware, W. O. Hibberson, and A. Major, "Safe Immobilization of High Level Nuclear Reactor Wastes," Proceedings of Symposium Scientific Advances and Community Risk, Australian Academy of Sciences, Canberra (1979).
120. A. E. Ringwood, S. E. Kesson, N. G. Ware, W. Hibberson, and A. Major, "Immobilization of High-Level Nuclear Reactor Wastes in SYNROC," Nature, 278, 219 (1979).

121. A. E. Ringwood, S. E. Kesson, N. G. Ware, W. Hibberson, and A. Major, "The SYNROC Process: A Geochemical Approach to Nuclear Waste Immobilization," Geochemical Journal (in press).
122. A. E. Ringwood and S. E. Kesson, "Immobilization of High-Level Wastes in Synroc Titanate Ceramic," Proceedings of Symposium Ceramics in Nuclear Waste Management, CONF-790420 (1979).
123. H. T. Larker, "Hot Isostatic Pressing for Consolidation and Containment of Radioactive Waste," Proceedings of Scientific Basis for Nuclear Waste Management, Boston, Plenum, NY (1979).
124. H. T. Larker, "Densification of Calcines and Direct Containment of Spent Nuclear Fuel in Ceramics by the ASEA Hot Isostatic Pressing Technique," Proceedings of Ceramics in Nuclear Waste Management, Cincinnati, CONF-790420, Technical Information Center, Oak Ridge, TN (1979).
125. W. Neumann and O. Kofler, "Coating of Waste Containing Ceramic Granules," Proceedings of Ceramics in Nuclear Waste Management, Cincinnati, CONF-790420, Technical Information Center, Oak Ridge, TN (1979).
126. W. Neumann, Coating of High Level Waste: Problems and Tasks (in German) SGAE-Report-2674 (1976).
127. E. Detilleux, H. Eschrich, and J. Van Geel, The Minerva Process. A Versatile Process for the Solidification of Liquid Radioactive Wastes from Nuclear Fuel Reprocessing, ETR-294 (1978).
128. O. Kofler and W. Neuman, Conditioning of HLW-Calcines, Part 1: Pyrocarbon Coating (in German), SGAE-Report-2864 (1977).
129. W. Neumann and O. Kofler, Conditioning of HLW-Calcines, Part 2: Nickel Coating (in German), SGAE-Report-2932 (1978).
130. J. Van Geel et al., "Incorporation of Solid High Level Wastes into Metal and Non-Metal Matrices," Proceedings of High-Level Radioactive Solid Waste Forms, NUREG/CP-0005, Denver, December 19-21, 1978, National Technical Information Service, Springfield, VA (1979).
131. L. Humblet and J. Van Geel, "Incorporation of Radioactive Solid Waste in Concrete-Polymer Material," British provisional patent application, No. 11849 (March 21, 1977).
132. K. Brichta and W. Neumann, Metal Embedding of Simulated HLW-Granules, (in German), SGAE-Report-2850 (1977).
133. W. Neumann, "Embedding Methods of Solidified Waste in Metal Matrices," Proceedings of Ceramics in Nuclear Waste Management, CONF-790420, Cincinnati, April 30-May 2, 1979, Technical Information Center, Oak Ridge, TN (1979).

134. W. S. Aaron, T. C. Quinby, and E. H. Kobisk, Cermet High Level Waste Forms, ORNL/TM-6404, Oak Ridge National Laboratory (June 1978).
135. E. Detilleux, H. Eschrich, and J. Van Geel, The Minerva Process, ETR-294 (1978).
136. J. Van Geel, H. Eschrich, and E. Detilleux, "Conditioning of Solid High Level Waste Products by Dispersion into Metal Matrices," AICHE Symposium Series, 72(154), 161 (1976).
137. J. Van Geel et al., "Solidification of High Level Liquid Wastes to Phosphate Glass-Metal Matrix Blocks," Proceedings of Management of Radioactive Wastes from the Nuclear Fuel Cycle, Vol. I, Vienna, March 1976, IAEA (1976).
138. IAEA, Techniques for the Solidification of High-Level Wastes, Technical Reports Series No. 176, p. 16, International Atomic Energy Administration, Vienna, Austria (1977).
139. W. Heimerl, "A Usable Method for the Management of High-Level Waste from Nuclear Fuel Reprocessing," Annals of Nuclear Energy, 4, 273 (1977).
140. J. E. Mendel and W. A. Ross, "The Chemical Durability of Glasses Containing Radioactive Fission Product Waste," (Abstract) Bull. Amer. Ceram. Soc. (April 1974).
141. G. J. McCarthy, "High-Level Waste Ceramics: Materials Considerations, Process Simulation, and Product Characterization," Nucl. Tech., 32(1), 10 (January 1977).
142. F. D. Roberts, G. H. Jenks, and C. D. Bopp, Radiation Effects in Solidified High-Level Wastes - Part 1. Stored Energy. BNWL-1944, Pacific Northwest Laboratory, Richland, WA (1976).
143. R. P. Turcotte, Radiation Effects in Solidified High-Level Wastes-Part 2, Helium Behavior. BNWL-2051, Pacific Northwest Laboratory, Richland, WA (1976).
144. W. J. Weber et al., "Radiation Damage in Vitreous and Devitrified Simulated Glass," Proceedings of Ceramics in Nuclear Waste Management, CONF-790420, Technical Information Center, Oak Ridge, TN (1979).
145. J. L. McElroy and W. A. Ross, "Alternative Solidified Forms for Nuclear Wastes" Proceedings of First Pacific Basin Conference on Nuclear Power Development and the Fuel Cycle. Ed. R. Farmakes, Honolulu, HI, October 1976, American Nuclear Society (1976).
146. W. S. Aaron, E. H. Kobisk, and T. C. Quinby, "Formation of Cermet High-Level Waste Forms for Repository Storage," Trans. Am. Nucl. Soc., 30, 284 (1978).

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