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THE EVALUATION AND SELECTION OF CANDIDATE HIGH-LEVEL WASTE FORMS

SAVANNAH RIVER OPERATIONS OFFICE
AIKEN, SOUTH CAROLINA

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ABSTRACT

Seven candidate waste forms being developed under the direction of the Department of Energy's National High-Level Waste (HLW) Technology Program, were evaluated as potential media for the immobilization and geologic disposal of high-level nuclear wastes. The evaluation combined preliminary waste form evaluations conducted at DOE defense waste-sites and independent laboratories, peer review assessments, a product performance evaluation, and a processability analysis. Based on the combined results of these four inputs, two of the seven forms, borosilicate glass and a titanate based ceramic, SYNROC, were selected as the reference and alternative forms for continued development and evaluation in the National HLW Program. Both the glass and ceramic forms are viable candidates for use at each of the DOE defense waste-sites; they are also potential candidates for immobilization of commercial reprocessing wastes. This report describes the waste form screening process, and discusses each of the four major inputs considered in the selection of the two forms.

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SUMMARY

Since early fiscal year 1979, the Department of Energy's Savannah River Operations Office has been the lead office for the National HLW Technology Program. The main task of the lead office has been to coordinate the development and evaluation of a number of candidate materials as potential media for the immobilization and geologic disposal of defense and commercial high-level nuclear wastes. Early screening evaluations during FY 1980, based on each form's performance potential and predicted process complexity, reduced the number of forms from an original seventeen to seven. The seven forms were borosilicate glass, high-silica glass, SYNROC (a titanate-based ceramic), tailored ceramic (an alumina-based ceramic), FUETAP concrete, glass marbles in a lead matrix, and coated particles produced by the sol- gel process. These forms underwent further development and characterization in FY 1980-81 to provide a data base for additional evaluations culminating in a screening assessment at the end of FY 1981, which is the topic of this report. From this assessment, borosilicate glass and a crystalline ceramic form based on the SYNROC concept were selected for further development.

Four major inputs formed the basis for the screening assessment: 1) waste-specific evaluations, 2) peer reviews, 3) a product performance evaluation, and 4) a processability analysis. Cost?

The first input was a series of waste-specific evaluations conducted by each of the DOE defense-sites, Savannah River, Hanford, and Idaho, to determine the preferred forms for immobilization of the HLW existing at each specific site. Additionally, two studies were conducted by Pacific Northwest Laboratory (PNL) to assess potential commercial HLW forms and processes. Borosilicate glass was consistently the highest rated form for immobilizing both defense and commercial HLW. Ceramic forms and other glass forms were the second most frequently preferred forms.

In addition to the waste specific evaluations, an Alternative Waste Form Peer Review Panel has convened annually since 1979 to review the relative scientific merits and engineering practicality of HLW forms being developed in the National Program. The Panel's most recent review in May, 1981 produced a relative ranking of the seven candidate forms. Borosilicate glass was rated as the preferred form for immobilization of HLW, followed in order by SYNROC, high-silica glass, tailored ceramic, coated particles, FUETAP concrete, and glass marbles in a lead matrix. The Panel felt that the crystalline ceramic form, SYNROC, was the best developed and characterized of the waste forms other than borosilicate glass.

A quantitative evaluation of waste form product performance, the third input, was performed by the Savannah River Laboratory

(SRL) using a rating system similar to one developed by a DOE Interface Working Group on HLW Form Selection Factors. The evaluation compared the seven candidate waste forms on the basis of leach resistance, waste loading, and mechanical stability, with leach resistance given the highest weight. Waste loading was calculated as volumetric curie content of SRP-HLW; mechanical stability was measured from standard impact tests at Argonne National Laboratory (ANL); and leach resistance was determined by use of standard leach testing procedures developed by the Materials Characterization Center (MCC). Leaching data were provided by the waste form developers, the MCC, and SRL.

Based on this evaluation, each waste form was assigned a merit rating, from which an approximate relative ranking of the seven candidate waste forms for product performance was derived. The waste forms divided into three groupings for the properties measured: 1) SYNROC, tailored ceramic and coated particles had the highest ratings; 2) borosilicate glass and high-silica glass had intermediate ratings; and 3) glass marbles in a lead matrix and FUETAP concrete ranked last. A clear delineation based on product performance could be made between the highest and lowest rated waste forms. However, because of uncertainties in the data and because of variations in relative leach rates of the waste forms for the different elements of interest, distinctions between waste forms in the high and intermediate categories were less clear. The ceramic forms rated highest because they had the lowest uranium leach rates, the highest weighted single property; however, the glass forms rated slightly better than the ceramics for cesium and strontium leach rates. Delineation among waste forms within a particular category was not possible.

The fourth input was a processability analysis conducted for SRL by the Engineering Department of E. I. du Pont de Nemours and Company. To quantitatively evaluate the waste form processes, twenty-one processability criteria were developed in four major categories; reliability/complexity, resource requirements, personnel safety, and quality control. Process data evaluated against these criteria were obtained from process flowsheets, equipment definitions, and conceptual facility layouts developed in collaboration with SRL and each of the waste form developers. The processability analysis yielded a clear delineation among the various processes. The final ratings suggested four general groupings of the processes. Borosilicate glass, the simplest process, and FUETAP concrete can be categorized as relatively simple; glass marbles in a lead matrix and high-silica glass as moderately complex; crystalline ceramics as complex; and coated sol-gel particles as very complex.

Waste form ratings from the product performance and processability evaluations were combined as geometric means to obtain

a combined ranking of the seven waste forms. The combined ranking in order of highest to lowest was: borosilicate glass, SYNROC and tailored ceramic, high-silica glass, FUETAP concrete, coated particles, and glass marbles in a lead matrix. Generally, waste forms with high product performance ratings had low processability ratings, and vice versa. Borosilicate glass achieved the highest combined rating because it had the highest processability rating combined with a good (intermediate) product rating. The two ceramic forms rated second overall, because their high product ratings compensated for their low processability ratings.

Based on the results of each of the evaluations described above, the Savannah River Operations Office recommended that the National HLW Technology Program be focused on (1) continued engineering scale-up of the borosilicate glass process and (2) further research, development, and characterization of an optimized crystalline ceramic waste form. Technical distinction between the two ceramic forms, SYNROC and tailored ceramic, was not possible. Therefore, it was decided to pursue an optimized ceramic form utilizing the expertise of both developers, Lawrence Livermore National Laboratory and Rockwell International.

The focal point of national waste form development efforts in FY 1982 will be the technology needs for the Defense Waste Processing Facility (DWPF) at Savannah River, currently scheduled as the first HLW immobilization plant in the U.S. Additionally, the glass and ceramic forms are candidates for use at other DOE defense-sites, and are potential candidates for immobilizing commercial reprocessing wastes should reprocessing of U.S. power reactor fuels be resumed. Both forms are thus considered to be applicable to the attainment of the overall goal of the National HLW Technology Program, which is to develop technology for immobilizing all U.S. defense and commercial high-level wastes.

INTRODUCTION

Background

As specified by Federal law,[1] the Department of Energy (DOE) has responsibility for providing for the isolation of U.S. nuclear wastes from the human environment. The Department is conducting comprehensive programs for the long-term management of radioactive wastes. The overall objective of these programs is to provide the required confinement of radioactive wastes 1) with minimum reliance on future human surveillance, and 2) in a way that ensures a high degree of isolation from the biosphere during the period of potential radiation hazard.

The DOE long-term waste management efforts are organized by nuclear waste category, specifically high-level waste (HLW), low-level waste (LLW), transuranic waste (TRU), and airborne waste. Specific DOE sites have been designated as "Lead Offices" to coordinate the development of the disposal technology for each waste type. Responsibility for coordinating the long-term management program for HLW which has been generated as a byproduct of national defense activities, or which may be generated from reprocessing of commercial spent power reactor fuels, resides with DOE's Savannah River Operations Office (DOE-SR).[2] Technical support and guidance to DOE-SR is provided by the Savannah River Laboratory (SRL), operated by E. I. du Pont de Nemours and Company.

The existing HLW in the United States is that generated in the nations's defense programs plus that generated during commercial reprocessing of spent fuel at the Nuclear Fuel Services (NFS) site in West Valley, New York from 1966 to 1971. Quantities of these wastes are listed in Table 1. They are now stored in underground tanks or bins at the defense sites at Hanford, Savannah River, and Idaho Falls, and at the NFS site at West Valley. Generation of reprocessing wastes continues at the defense sites. The spent fuel elements from commercial power reactors are potentially a much larger source of reprocessing waste, should power reactor fuel reprocessing be resumed in the United States.

Program Strategy

The High-Level Waste Technology Program was established in fiscal year (FY) 1979 to develop the technology for immobilizing HLW into solid waste forms which will provide highly efficient barriers against radionuclide release to the environment during interim handling and terminal storage. The strategy for HLW immobilization involves 1) the development of technology to support the choice of an isolation system for each DOE defense HLW site and for any commercial HLW site, 2) development of candidate waste forms and

TABLE 1

U.S. HIGH-LEVEL NUCLEAR WASTES

Source	Type	1980 Quantities			1990 Quantities
		$10^3 m^3$	Tanks	Megacuries	Megacuries
Hanford Plant	Alkaline	183	156	200	400
	Cs/Sr Sources	-	-	358	395
Idaho Chemical Processing Plant	Acid	9.3	9	17	16
	Calcine	2.1	3	37	95
Savannah River Plant	Alkaline	96.7	33	700	862
Nuclear Fuel Services	Alkaline	2.1	1	37	30
	Acid	0.04	1	1.6	1.3
Spent LWR Fuel	Not Processed	-	-	10,400	35,000

production processes, and 3) support of R&D activities required to construct and operate the facilities for immobilizing DOE defense HLW.

In response to recommendations by the Interagency Review Group (IRG) on Nuclear Waste Management[3] and the National Academy of Sciences,[4] a variety of different waste forms have been defined and developed to permit flexibility in the immobilization and terminal storage systems. The milestones for the national program tasks related to waste form development activities were established as follows:

1. The development and characterization of all viable candidate forms during FY's 1979-1981.

2. The selection of two waste forms at the end of FY 1981 for further development.

3. Further development, characterization, and evaluation of these two forms during FY's 1982 and 1983.

4. Selection of one final form before the end of FY 1983 for the Defense Waste Processing Facility (DWPF), to be located at the Savannah River Plant (SRP) site as the first immobilization facility in the U.S.

On August 1, 1981, a screening of seven candidate waste forms was completed to satisfy the program milestone of selecting two final forms by the end of FY 1981. Four major inputs served as the bases for the selection of the final two forms.

1. Preliminary waste form evaluations conducted to determine the preferred forms for immobilization and geologic disposal of HLW. These previously documented studies were performed at each of the DOE defense sites, as well as at independent laboratories for defense and commercial HLW, respectively.

2. A series of annual reviews of the candidate waste forms being developed in the National HLW Technology Program. These previously documented reviews were conducted by the Alternative Waste Form Peer Review Panel.

3. A quantitative evaluation of waste form product performance based on comparative characterization data available on or before August 1, 1981 for the seven candidate waste forms.

4. A quantitative evaluation of the various processes required to produce the seven candidate waste forms. Details of this study will be reported in a forthcoming report to be issued by the Savannah River Laboratory.

The final decision for selecting one waste form for the DWPF, the initial high-level waste immobilization facility in the U.S., will be made before the end of FY 1983. Factors that will be considered in addition to those presented in this document, will be further product performance comparisons, comparative risk assessments, and comparative cost analyses. Assessments of each form's ability to conform with postulated regulatory, repository, and waste package criteria will also be made.

This report documents the FY 1981 waste form screening process, describes the seven candidate forms, and discusses the four major decision inputs and the selection of the final two waste forms.

CANDIDATE HIGH-LEVEL WASTE FORMS

Since the inception of the national program in May 1979, seventeen candidate waste forms have been developed and characterized by fourteen participating contractors, as potential media for the geologic disposal of high-level nuclear wastes (Table 2). The broad-based research efforts have been conducted at the waste processing sites, DOE national laboratories, industrial laboratories, and universities. Research and development activities for ten of the forms were terminated at various stages of the program based on preliminary reviews which raised technical concerns about the viability of these forms as candidates for geologic disposal of wastes. Following continued development and characterization, the seven remaining forms (Table 3) have undergone further evaluations to satisfy the national program objective of selecting, at the end of FY 1981, two forms for advanced development in support of the DWPF project and in support of the overall program goal of immobilizing all HLW existing in the United States.

The following are descriptions of the seven final forms evaluated. Because performance data were obtained from forms containing simulated SRP waste, the product and process descriptions presented below apply specifically to immobilizing SRP HLW. Other waste types would affect specific waste form composition and possibly processing as well. In the production processes for all of the waste forms except the crystalline ceramics, aluminum is removed from the waste prior to solidification. Aluminum, a desirable component for producing the crystalline ceramics, is not removed from the waste when producing these forms. Because of this difference, the waste loadings in the descriptions of the crystalline ceramic forms would be somewhat lower on a comparable basis with the other forms.

Borosilicate Glass.

Borosilicate glass[5] is the best developed waste form of all candidate forms for high-integrity radionuclide containment. Typically, a borosilicate waste glass consists of about 20-35% waste oxides (with Al removal), 40-50% silica, 5-10% boron oxide and 10-15% alkali oxides, plus other additives. Formation temperatures for these compositions are in the range of 1050-1150°C. The reference process involves feeding a slurry waste stream and glass additives to a continuous joule-heated glass melter, from which the waste glass is poured into its final form in 2 ft diameter by 10 ft canisters approximately 80% full.

TABLE 2.

CANDIDATE WASTE FORMS CONSIDERED FOR GEOLOGIC DISPOSAL OF HIGH-LEVEL WASTE

Waste Form	Developer/Contractor
Borosilicate Glass	Savannah River Laboratory Pacific Northwest Laboratory
High-Silica Glass	Catholic University of America NPD Nuclear Systems, Inc.
Phosphate Glass	Pacific Northwest Laboratory Brookhaven National Laboratory
Clay Ceramic	Rockwell Hanford Operations Pacific Northwest Laboratory
Glass Ceramic	Idaho Chemical Processing Plant
Tailored Ceramic	Rockwell International Pennsylvania State University
SYNROC	Lawrence Livermore National Laboratory Argonne National Laboratory North Carolina State University
Titanate Ion Exchanger	Sandia National Laboratory
Stabilized Calcine	Idaho Chemical Processing Plant
Pelletized Calcine	Idaho Chemical Processing Plant
Normal Concrete	Savannah River Laboratory Oak Ridge National Laboratory Pennsylvania State University
Hot-Pressed Concrete	Pennsylvania State University
FUETAP Concrete	Oak Ridge National Laboratory
Matrix Forms	Pacific Northwest Laboratory Argonne National Laboratory
Coated Sol-Gel Spheres	Oak Ridge National Laboratory
Cermet	Oak Ridge National Laboratory
Disc-Pelletized Coated Particles	Pacific Northwest Laboratory Battelle Columbus Laboratory

TABLE 3.

SEVEN CANDIDATE WASTE FORMS EVALUATED FOR GEOLOGIC DISPOSAL OF HIGH-LEVEL WASTES

Waste Form	Developer/Contractor
Borosilicate Glass	Savannah River Laboratory Pacific Northwest Laboratory
SYNROC	Lawrence Livermore National Laboratory Argonne National Laboratory North Carolina State University
Tailored Ceramic	Rockwell International Pennsylvania State University
High-Silica Glass	Catholic University of America NPD Nuclear Systems, Inc.
FUETAP Concrete	Oak Ridge National Laboratory
Coated Sol-Gel Particles	Oak Ridge National Laboratory
Glass Marbles in a Lead Matrix	Pacific Northwest Laboratory

High-Silica Glass.

High-silica natural glasses (obsidians and tektites) are known to have persisted for long periods in both terrestrial and lunar environments. However, these glasses are formed at temperatures of 1600-1800°C — high enough to vaporize ruthenium and cesium radionuclides present in HLW. The key to the development of this form has been the low-temperature Porous Glass Matrix process[6] which provides a means for fabricating high-silica waste forms at 1200°C by sintering an intimate mixture of porous glass frit and waste calcine. The form is produced by a rising level, in-can sintering process in which porous glass powder (10-300 μm diameter grains with 0.01 μm pores) is blended with waste calcine and charged under vacuum into an inductively heated canister. Pores in the glass grains collapse at 600-900°C to trap volatiles, followed by sintering of the frit and waste particles at about 1100°C. Typically, the high-silica waste glass will contain from 50-60% silica at a waste loading of approximately 20-30% waste oxides (with Al removal).

SYNROC.

SYNROC[7] is a densely consolidated, titanate-based, polyphase crystalline ceramic form in which radionuclides are incorporated as dilute solid solutions in the crystal lattices of perovskite, zirconolite, and either hollandite, nepheline, or pollucite. "SYNROC-D", a particular variation of this waste form developed for the immobilization of SRP high-level wastes is formed from tailored additions of TiO_2, ZrO_2, SiO_2, CaO, and perhaps other oxides, to the waste sludge. In the reference SYNROC process, an intimately blended mixture of waste and additives is calcined, tamped into a canister, preheated under vacuum, and then hot isostatically pressed (HIPped) at 1100-1200°C and 25,000 psi, to synthesize the mineral phases. Waste loadings of 50-70 wt % (as oxides, without Al removal) have been achieved. Potentially, the form may be produced via hot-pressing or sintering.

Tailored Ceramic.

Tailored ceramic[8] is a densely consolidated, alumina-based, polyphase crystalline ceramic material developed for SRP waste. It is formed by tailored additions of Al_2O_3, SiO_2, rare earth, and perhaps other oxides, to the waste sludge. The waste components are incorporated into stable crystalline phases such as uraninite, magnetoplumbite, spinel, corundum, nepheline and perovskite. The reference process for production of the tailored ceramic waste form is identical to that required for fabrication of the SYNROC waste form. Waste loadings of 50 to 90 wt % (as oxides,

without Al removal) have been achieved, depending on waste composition.

FUETAP Concrete.

Concretes formed under elevated temperatures and pressures (FUETAP concretes)[9] are prepared from common Portland cements, fly ash, sand, clays, and waste calcines. The production process for this form involves dry blending the cement additives with the waste calcines, followed by wet blending with the addition of water. This mixture is poured into 2 ft diameter by 10 ft canisters and cured under mild autoclave conditions (100°C, 1 atm steam). Subsequently, the concrete is dewatered under vacuum at 250°C for 24 hours. Typically, the FUETAP concrete waste form has a 20 wt % waste loading (with Al removal).

Coated Sol-Gel Particles.

Coated sol-gel particles[10] are 750-micron zirconia-based ceramic spheres enclosed in three separate coatings. The inner coating is low-density silicon carbide; the middle coating is high-density silicon carbide; and the outer coating is high-density pyrolytic carbon. In the sol-gel process, matrix elements are added to a solution of waste sludge dissolved in nitric acid, followed by urea addition to neutralize excess acid. A chilled solution (~0°C) of HMTA (hexamethylenetetramine) is added to the urea feed mixture and fed through a vibrating nozzle into an immiscible liquid at 55°C to form the sol-gel spheres. After aging, rinsing, and washing, the spheres are transferred to fluidized beds for application of the coating layers by chemical vapor deposition (CVD). The coated spheres then would be packaged together with an inorganic binder (probably an aluminate or silicate-aluminate compound) into a canister to obtain the final waste form. A canister would contain approximately 10^8 spheres. Single uncoated particle waste loadings of from 70-90 wt % (with Al removal) have been achieved. The net canister waste loading considering coating volumes and canister void spaces is about half the single-particle waste loading.

Glass Marbles in a Lead Matrix.

Glass marbles in a lead matrix[11] provide an alternative to the production of large canisters of glass. Molten glass similar to the borosilicate glass composition, with approximately 28 wt % waste calcine, is cast into marbles 1.3 cm in diameter. The marbles are batch-loaded into a canister and the void space is

filled with a low-melting lead-tin alloy in the form of shot. The canister is then zone heated in an induction furnace to melt the shot and provide a continuous metal phase matrix which solidifies from the bottom upward. Only about 60% of the volume of a 2 ft diameter by 10 ft canister would be occupied by the glass marbles, giving a significantly lower net canister waste loading than for a cansiter of glass.

PRELIMINARY WASTE FORM EVALUATIONS

Introduction and Summary

Separate evaluations were conducted at each of the DOE defense sites, Savannah River (near Aiken, South Carolina), Hanford (near Richland, Washington), and the Idaho Chemical Processing Plant (near Idaho Falls, Idaho), to determine the preferred solid forms for immobilization of existing defense HLW at each location. The individual evaluations rated from eight to nineteen candidate waste forms according to process complexity and potential product performance. All of the evaluations weighted product and process approximately equally. Similar independent assessments were sponsored by the Pacific Northwest Laboratory (PNL) for immobilization of nuclear wastes from reprocessing of commercial power reactor spent fuel. The first of two studies investigated product durability, and the second evaluated potential production processes.

The preliminary evaluations employed a significant amount of technical judgment and were based somewhat on qualitative or non-standardized quantitative data. However, each study evaluated the various forms and processes on the best information available at the time. Although continuing research and development has refined and changed the forms and processes, these early evaluations were valuable screening studies. They identified unacceptable waste forms and directed development efforts towards the most promising alternatives for waste immobilization. Additionally, while significant revisions in the waste forms and processes have been made, the changes have not been so drastic as to negate the results and conclusions reported in the preliminary studies. The most recent evaluations of product performance and waste form processability for the seven candidate waste forms are based on current comparative data, as discussed in the following sections of this report.

The results of the waste-site and independent product and process evaluations exhibit several important and consistent trends.

- In each evaluation by the DOE defense-sites, borosilicate glass consistently scored the highest and was selected as a viable and preferred form for immobilization of HLW. Similarly, glass was rated highest in both commercial waste form evaluations.

- Generally, waste forms had either low product ratings and high process ratings, or high product ratings and low process ratings. Glass forms always had high process ratings and good product ratings.

- The second most preferred form was a ceramic, usually a crystalline ceramic. These forms exhibit product characteristics potentially superior to glass forms, but require comparatively complex processes.

- Concrete forms generally had good processing ratings (although lower than glass), but demonstrated some of the poorest product performance characteristics.

Defense Waste Form Evaluations

Savannah River.

A study[12] conducted by the Savannah River Laboratory (SRL) evaluated eleven waste forms (borosilicate glass as the reference form, plus ten alternatives) that had been proposed for solidification of SRP high-level waste (Table 4). The goal of this preliminary evaluation was to select a limited number of forms for more detailed studies. At the time of the evaluation, most of the waste forms lacked detailed experimental data for the factors upon which they were evaluated. Information on each form was obtained from published articles and reports, supplemented by discussions with the proponents of the forms and technical judgments made to develop the waste form comparison.

The alternative forms evaluated were selected because of their potential for improved overall performance relative to borosilicate glass. Twelve factors (7 product and 5 process) weighted relative to their overall importance were considered for each form. Leachability and long-term stability were the most important product performance concerns, while process complexity outweighed other process factors. Each particular factor was rated for each form on a scale from 1 to 5 (with 5 being best). The factors, weights, and final numerical scores are shown in Table 5. The weighted sum of product factors provided a relative ranking of potential product quality. The weighted sum of process factors provided a relative ranking of the processes (mostly conceptual) for producing each form. Overall ratings were obtained by adding the product and process scores. The major conclusions of the evaluation were:

- Borosilicate glass had the highest overall score of all the forms considered

- Six waste forms had potentially better product properties than borosilicate glass

- Coated waste forms had the highest product scores but were poorest in process characteristics

TABLE 4.

CANDIDATE WASTE FORMS EVALUATED FOR IMMOBILIZATION OF SAVANNAH RIVER PLANT HIGH-LEVEL WASTE

Borosilicate Glass

High-Silica Glass

FUETAP Concrete

Hot-Pressed Concrete

Supercalcine Ceramic

SYNROC

Cermet

Glass Marbles in a Metal Matrix

Ceramic Pellets in a Metal Matrix

Coated Ceramic

Coated Ceramic via Sol-Gel

TABLE 5.

Results of Evaluation of Candidate Forms For Immobilization of Savannah River Plant High-Level Waste.

	PRODUCT FACTORS								PROCESS FACTORS						
	Development Status	Waste Loading	Leachability	Long-Term Stability	Thermal Conductivity	Thermal Stability	Transportation Safety	WEIGHTED SUM	Complexity	State of Development	Quality Assurance	Yield and Recycle	Process Safety	WEIGHTED SUM	OVERALL SCORE
Borosilicate Glass	5	3	3	3	2	5	4	66	4	5	3	3	4	69	135
High-Silica Glass	2	2	5	3	2	5	4	68	3	2	3	2	4	51	119
FUETAP Concrete	3	1	1	2	2	2	2	33	5	4	3	2	4	69	102
Hot-Pressed Concrete	2	3	1	4	2	3	3	49	3	1	3	2	3	45	94
Supercalcine Ceramic	2	5	4	5	2	5	5	81	2	1	1	1	3	30	111
SYNROC Ceramic	3	5	4	5	2	5	5	83	2	1	1	1	2	27	110
Cermet (Urea Process)	2	3	3	1	2	5	5	52	1	2	5	1	2	36	88
Glass Marbles in Metal Matrix	4	2	3	3	3	4	2	57	3	4	4	3	3	60	117
Ceramic Pellets in Metal Matrix	3	4	4	3	4	4	3	67	2	2	2	1	3	36	103
Coated Ceramic	3	4	5	5	2	5	5	86	2	2	2	1	2	33	119
Coated Ceramic via Sol-Gel	1	4	5	5	2	5	5	82	2	3	2	1	4	42	124
FACTOR WEIGHTS	2	2	5	5	1	2	2		6	3	3	3	3		

- Concrete waste forms had the poorest product scores, but were rated highly on process characteristics.

Hanford.

← Schulz RHO ST32

At the Hanford site, a preliminary evaluation[13] of solid waste forms for immobilization of Hanford high-level defense wastes was conducted using published articles, reports, and conference proceedings. Additional data were obtained from detailed discussions with scientists and engineers involved in developing the various forms. Nineteen different waste forms (including the 11 forms considered at Savannah River) were evaluated and compared to determine their applicability and suitability for immobilization of Hanford salt cake, residual liquid, sludges, and mixtures thereof (Table 6). Because the final plan for long-term management of Hanford HLW has not yet been formulated, the assessment was structured to take into account several alternative immobilization senarios. These were (1) near-term retrieval of all in-tank wastes with and without radionuclide removal, (2) in situ disposal of in-tank wastes, and (3) near-term retrieval of only residual liquid with and without radionuclide removal. The objective of this assessment was to identify those waste forms and processes meriting further research and development to qualify them for consideration in the final selection of waste forms for fixation of Hanford HLW.

The evaluation technique was similar to that implemented in the Savannah River evaluation. Fourteen factors (7 product and 7 process) weighted relative to their overall importance were considered for each form (Table 7). Leachability, long-term stability, and waste loading were the most important criteria for waste form performance, while process simplicity was the most important process characterisitic. Every waste form was given a rating of 1 to 5 (5 being best) for each factor. The numerical scales were adjusted so that the maximum possible product, process, and overall (sum) ratings were 50, 50, and 100, respectively. The final waste form rankings and scores for three waste types are shown in Table 8. (Bulk, in situ disposal results are not considered since they are not related to geologic disposal).

Two general conclusions were made from the final waste form selections and rankings.

- Borosilicate glass is a viable waste form for fixation of all types of Hanford high-level wastes.

- No one waste form was distinctly superior to any other. Waste forms typically exhibited either high product and low process scores, or low product and high process scores. Borosilicate

TABLE 6.

CANDIDATE WASTE FORMS EVALUATED FOR IMMOBILIZATION OF VARIOUS HANFORD HIGH-LEVEL WASTES

Ceramics

- Supercalcine Ceramic
- SYNROC
- Tailored Ceramic
- Clay Ceramics - Monoliths/Marbles
- Aqueous Silicate

Concrete

- Supergrout Concrete
- Sludge in Concrete
- FUETAP Concrete
- Hot-Pressed Concrete

Multibarrier

- Glass in Metal Matrix
- Ceramic Pellets in Metal Matrix
- Ceramic in Concrete
- Coated Ceramic
- Cermet

Glass

- Borosilicate Glass - Monoliths/Marbles
- Porous Glass Matrix (High-Silica Glass)
- Glass-Ceramics - Monoliths/Marbles

Miscellaneous

- Calcine
- Bitumen

TABLE 7.

WASTE FORM PRODUCT AND PROCESS CRITERIA USED TO EVALUATE CANDIDATE FORMS FOR IMMOBILIZATION OF HANFORD HIGH-LEVEL WASTES

Waste Form Product Criteria	Weight %
Waste Loading	23.8
Leachability	28.6
Repository Environment/Waste Form Interaction	19.0
Thermal Stability	9.5
Radiation Stability	9.5
Mechanical Stability	4.8
Fire Resistance	4.8

Waste Form Process Criteria	Weight %
Simplicity	28.6
Scale-up Potential	19.0
Remotability	19.0
Process Safety	19.0
Quality Assurance	4.8
Rework Capacity	4.8
Status of Development	4.8

TABLE 8.

RESULTS OF EVALUATION OF CANDIDATE FORMS FOR IMMOBILIZATION OF HANFORD HIGH-LEVEL WASTES

Waste Type	Ranking	Numerical Score	Waste Form
Sludge with Radionuclide concentrate	1	72	Coated Ceramics
	2	70	Borosilicate Glass - Marbles
	3	70	Ceramic Pellets in Metal Matrix
	4	70	Tailored Ceramic
	5	70	Supercalcine Ceramic
	6	70	Borosilicate Glass - Monoliths
	7	70	SYNROC
Residual Liquid	1	70	Borosilicate Glass - Monoliths
	2	69	Borosilicate Glass - Marbles
	3	66	Bitumen
Radionuclide Concentrate From Residual Liquid	1	72	Borosilicate Glass - Monoliths
	2	70	Borosilicate Glass - Marbles
	3	68	Glass in Metal Matrix

glass had average rating values for both product and process properties.

The waste forms listed in Table 8 were selected as the preferred forms for further research and development for the immobilization of Hanford high-level wastes, and are thus the candidates for Hanford's final waste form selection.

Idaho Chemical Processing Plant

Two separate evaluations were conducted to assess potential waste forms for immobilization of Idaho Chemical Processing Plant (ICPP) high-level waste calcines.

Independent Review Panel Evaluation

The first evaluation was performed by an independent review panel[14] chartered to provide Exxon Nuclear Idaho Company with objective recommendations on the most promising waste forms for final disposal of ICPP calcined wastes. The panel, chaired by R. G. Post of the University of Arizona, was composed of 7 scientists and engineers in the disciplines of geochemistry, materials science, chemical engineering, nuclear engineering, and inorganic chemistry. The four categories of waste forms evaluated by the panel were glass, glass ceramic, tailored (crystalline) ceramic, and composites. The last category, composites, consisted of one of the previous forms or calcine, in granular size, in a matrix material such as concrete or metal. The full range of materials that were considered are listed in Table 9.

The waste forms were evaluated based on 11 product, 8 process, and 5 systems-development criteria, with these categories weighted 50%, 40%, and 10%, respectively. The latter category refers to the relationship of a waste form to the entire disposal system. A complete list of the criteria in each category is shown in Table 10. In contrast to the other site evaluations, the most heavily weighted product criteria were transportation handling safety (dispersal) and transportation handling safety (temperature). Remote operation capability and engineering feasibility were the most important process criteria, while feasibility, timing/cost, and environmental impact were weighted heaviest in the system development criteria.

The rating method employed by the panel used rating numbers that were exponents rather than simple terms or factors. Each candidate material was compared to a reference material, which for this evaluation was in-can melt borosilicate glass. If the candidate form was considered to be better than the reference

TABLE 9.

CANDIDATE WASTE FORMS EVALUATED FOR IMMOBILIZATION OF IDAHO CHEMICAL PROCESSING PLANT HIGH-LEVEL WASTE CALCINES

Calcine	Composite: Solids in FUETAP Concrete Matrix
Stabilized Calcine	Calcine Marbles
Calcine Marbles	Glass Marbles
	Glass Ceramic Marbles
	Sintered Ceramic
	Hot Press Ceramic
	Stabilized Calcine

Glass	Composite: Solids in Cement Hot Press Matrix
In-can Melt	Calcine Marbles
Continuous Melt	Glass Marbles
Marbles	Glass Ceramic Marbles
	Sintered Ceramic
	Hot Press Ceramic
	Stabilized Calcine

Glass Ceramic	Composite: Solids in Cast Metal Matrix
Melt-Monolith	Calcine Marbles
Melt-Marbles	Glass Marbles
Sintered Monolith	Glass Ceramic Marbles
Sintered Marbles	Sintered Ceramic
	Hot Press Ceramic

Tailored Ceramic	Composite: Solids in Sintered Metal Matrix
Hot Press Marbles	Calcine Marbles
Hot Press Monolith	Glass Marbles
Sintered Marbles	Glass Ceramic Marbles
Sintered Monolith	Sintered Ceramic
	Hot Press Ceramic
	Stabilized Calcine

TABLE 10.

WASTE FORM CRITERIA USED TO EVALUATE CANDIDATE FORMS FOR IMMOBILIZATION OF IDAHO CHEMICAL PROCESSING PLANT HIGH-LEVEL WASTE CALCINES

Product Criteria

- Waste Loading
- Leachability - Short Term, Long Term
- Chemical Stability - Short Term, Long Term
- Mechanical Stability - Long Term
- Thermal Stability - Short Term
- Transportation Handling Safety - Dispersal
- Transportation Handling Safety - Temperature
- Characterization Development Status
- Multifeed Uniformity

Process Criteria

- Preprocess Treatment
- Engineering Feasibility
- Reliability/Maintainability
- Quality Assurance
- Recycle Capability
- Adaptation to Multifeed
- Remote Operation Capability
- Safety

System Development

- Feasibility
- Demonstration
- Environmental Impact
- Industrial Base
- Timing/Cost

material for a particular factor, it was given a positive rating representing the power of two by which it was better. If it was twice as good it was given a rating of 1; if four times as good, a rating of 2. Similarly, if a candidate form was only 1/4 as good, or four times worse, it received a rating of -2.

The final consensus of the review panel for the preferred waste forms for immobilization of ICPP-HLW is shown in Table 11. The Panel concluded that eight waste forms could prove satisfactory. These waste forms are all varations of the three categories of forms in Table 11. Although stabilized calcine in a concrete matrix had a slightly higher numerical rating, the panel felt that borosilicate glass was the best choice because its performance is acceptable, its process is well developed, and it could be implemented expeditiously. At the time of the evaluation, the in-can melt process was considered the best. However, the panel acknowledged that future development could result in the continuous melt process being superior. The panel also concluded that the matrix form could prove acceptable. However, they felt that development was not sufficiently advanced to provide confidence, and that the rating was based on sparse experimental evidence.

Exxon Nuclear Idaho Company Evaluation

The second evaluation[15] was conducted by Exxon Nuclear Idaho Company (ENICO) to determine the potential suitability of several candidate crystalline materials for immobilization of high-level ICPP zirconia waste calcines. The waste forms included titanate-based and tailored ceramics, glass ceramics, and matrix composites. The ceramic forms were considered potentially to offer all the favorable properties of glass, plus increased density, lower leachability, improved thermal stability, and improved long-term stability.

The various forms were evaluated on the basis of five product performance and three process properties. Those properties considered for product performance were: available crystalline phases for radionuclide entrapment, relative leach resistance, density, calcine loading, and sensitivity to compositional variation. Required process steps, firing temperature, and firing schedule complexity were considered for the processes.

The evaluation concluded that information available at the time of the study was insufficient to establish any definitive advantages of the ceramics over glass. Although potential advantages exist for ceramic waste products, considerable time and research would be required to develop a ceramic product with overall product and process properties comparable to glass.

TABLE 11.

RESULTS OF EVALUATION OF CANDIDATE FORMS FOR IMMOBILIZATION OF IDAHO CHEMICAL PROCESSING PLANT HIGH-LEVEL WASTE CALCINES

Waste Form	Numerical Rating	Comments
Borosilicate Glass	49 - In-Can Melt 45 - Continuous Melt	Glass is First Choice
Stabilized Calcine	51 - FUETAP Matrix 43 - Metal Matrix	Process Not Sufficiently Developed for Confidence
Tailored Ceramic	38 - Sintered Monolith	Offer Superior Performance. More R & D Needed.

However, based on the limited information collected in the evaluation, a glass ceramic (although not as suitable as glass) appears potentially more suitable to immobilize ICPP calcine waste than do the more highly crystalline or tailored ceramic forms or the matrix forms. The glass ceramic forms appear to accommodate a wider range of calcine loading, and are less affected by compositional variation. Additionally, concretes and grouts were felt to be potentially suitable for physically encapsulating ICPP calcines, but the applicability of such matrices could be highly dependent on regulatory and repository criteria.

Commercial Waste Form Evaluations

Waste Form Product Durability.

The potential product durability of ten candidate commercial waste forms was investigated experimentally at Pacific Northwest Laboratory (PNL).[16] In the absence of standard and comparable experimental data, the characterization study applied uniform volatility, mechanical strength, and leach tests to candidate forms. Additionally, bulk property, phase composition, and microstructural examinations were conducted on the simulated waste products. Waste loading varied from 5% to 100% . The waste forms investigated are listed in Table 12. Nine of the waste forms were produced from a simulated PW-9 high-sodium calcine.[17] The glass form, PNL 76-68, was prepared from a simulated PW-8a calcine[17] which had a higher sodium and iron content.

Although ten waste forms were fabricated for comparative testing, not all tests could be applied to all materials. Hot-isostatically pressed materials were reported to crack extensively during preparation, and suitable specimens could not be obtained for mechanical testing. Volatility evaluations during fabrication were not performed on all forms because of process equipment considerations, and hot-pressed PW-9 calcine samples were observed to shatter spontaneously. Leach tests, however, were conducted on all materials.

The two-part conclusions of this study were based on (1) an analysis of bulk properties and waste loading, and (2) product durability. The 100% PW-9 waste forms required the least volume and total weight, while the cement waste forms had a low density, had a low waste loading, and required the highest volume and weight. Product volume and weight become important parameters when considering canister material costs or repository capacity. Glass, glass-ceramic, and supercalcine[18] forms ranked highest in waste form durability. The 100% PW-9 calcine waste forms ranked lowest in durability. However, PW-9 waste form durability was improved by the addition of 50% glass frit. Additionally, waste-matrix

TABLE 12.

CANDIDATE WASTE FORMS EVALUATED FOR IMMOBILIZATION OF COMMERCIAL HIGH-LEVEL WASTES

Cold Pressed and Sintered PW-9 Calcine

Hot Pressed PW-9 Calcine

Hot Isostatic Pressed PW-9 Calcine

Cold Pressed and Sintered SPC-5B Supercalcine

Hot Isostatic Pressed SPC-5B Supercalcine

Sintered PW-9 and 50% Glass Frit

Glass 76-68

Celsian Glass Ceramic

Type II Portland Cement and 10% PW-9 Calcine

Type II Portland Cement and 10% SPC-5B Supercalcine

interactions in the cement based waste forms were reported to give undesirable partitioning of fission products among primary cementitious phases.

Waste Form Process Evaluation.

An independent engineering study and comparative evaluation of eleven candidate processes for the solidification and isolation of high-level liquid waste from processing of irradiated commercial power reactor fuel was conducted for PNL by E. R. Johnson Associates, Inc.[19] The purpose of the study was to assess various processes in the context of the feasibility of establishing practical production-scale facilities in a highly radioactive environment requiring remote operation and maintenance. The processes evaluated (Table 13) were selected based on reported physical and chemical properties of eleven promising candidate waste forms. An earlier PNL study[20] presented preconceptual process designs that served as bases for the subsequent evaluations and comparisons. This information was supplemented by original data and other process information in the published literature.

To evaluate the processes, twelve criteria were identified and arranged into six principal criteria, which were then subdivided into twenty-two subcriteria and assigned weighting factors. The six major criteria categories and their relative weightings are shown in Table 14. The two most heavily weighted areas were related to process complexity, which may be the most crucial factor in the remote production of nuclear waste forms, and safety, which is a prime requirement for any process. Each process was assigned a score of 1 to 10 for each of the subcriteria. Overall process ratings were obtained by summing the products of the subcriteria ratings and the subcriteria weights.

The final results of the evaluation are given in Table 15. The processes judged to have the greatest potential were those for making glass, either by in-can melting or joule-heated melting. In all of the principal criteria categories, in-can melting, joule-heated melting, glass ceramic, and concrete processes were generally highest rated. This trend was a result of 1) the relative simplicity and safety of these waste form processes, 2) the available technology and pilot plant experience for each of the processes, and 3) the potential facility requirements for housing each of the processes. Conversely, the other waste form processes generally required more complex equipment, were in a laboratory stage of development, posed greater safety hazards, had limited quality assurance capabilities, and required significantly larger facilities.

TABLE 13.

CANDIDATE WASTE FORM PROCESSES EVALUATED FOR IMMOBILIZATION OF COMMERCIAL HIGH-LEVEL WASTES

In-Can Glass Melter

Joule-Heated Glass Melter

Glass Ceramic

Marbles-in-Lead

Supercalcine Pellets-in-Metal

Carbon-Coated Pellets-in-Metal

Supercalcine, Hot-Isostatic Pressed

SYNROC, Hot-Isostatic Pressed

Titanate

Concrete

Cermet

TABLE 14.

CANDIDATE COMMERCIAL WASTE FORM PROCESS EVALUATION CRITERIA

Principal Criteria	Number of Subcriteria	Total Weighting Factor Points
Complexity of Process	7	60
Safety	3	40
Development Work Required	3	35
Process Requirements	5	25
Facility Requirements	2	20
State of Development	2	20

TABLE 15.

FINAL PROCESS RATINGS FOR COMMERCIAL WASTE FORM PROCESS EVALUATION

Waste Form Process	Ranking	Rating Score
In-Can Glass Melter	1	1770
Joule-Heated Glass Melter	2	1490
Glass Ceramic	3	1400
Concrete	4	1293
Marbles-in-Lead	5	1176
Titanate	6	891
Cermet	7	808
Supercalcine Pellets-in-Metal	8	794
Carbon-Coated Pellets-in-Metal	9	719
Supercalcine, Hot Isostatic Pressed	10	640
SYNROC, Hot Isostatic Pressed	11	470

ALTERNATIVE WASTE FORM PEER REVIEW PANEL EVALUATIONS

Introduction and Summary

The second major input considered in the waste form evaluation and selection process was a series of annual independent assessments of the various waste forms being developed in the National HLW Technology Program. These reviews were conducted by the Alternative Waste Form Peer Review Panel chaired by Dr. L. L. Hench of the University of Florida. The Panel is composed of eight scientists and engineers (Table 16) representing independent, non-DOE laboratories from industry, government, and universities; and the disciplines of materials science, ceramics, glass, metallurgy, and geology. It has the assignment of evaluating and reviewing the relative scientific merits and engineering practicality of candidate waste forms for geologic disposal of high-level radioactive wastes. The Panel has convened annually for three years beginning in August 1979, to review candidate forms being developed under the direction of the HLW Technology Program Lead Office. To facilitate each assessment the most current data, reports, and other information available for each waste form were provided by the waste form developers for distribution to the Panel members. Additionally, for the second and third evaluations by the Panel, program reviews were conducted at which the waste form developers presented their most recent results from the ongoing research and development efforts.

The third review of candidate waste forms conducted by the Panel in May 1981, provided a consensus ranking of the seven candidate forms (Table 17). Borosilicate glass was ranked highest followed by SYNROC, high-silica glass, tailored ceramic, coated particles, FUETAP concrete, glass marbles in a lead matrix, and thermal spray coated glass and ceramic marbles. The ranking of the forms, the discussions of their advantages and disadvantages, and the recommendations for future research and development were given significant consideration in the selection of the two final candidate waste forms.

Evaluation Numbers 1 and 2

The first two reviews[21,22] of candidate waste forms were conducted in August 1979 and May 1980. The first review evaluated the relative merits and potential of eleven candidate forms; the second considered fifteen forms. More waste forms were considered in the second review because the general category of multibarrier forms was expanded to include five specific multibarrier forms. The 1980 review also assessed four potential approaches to presolidification processing.

TABLE 16.

ALTERNATIVE WASTE FORM PEER REVIEW PANEL

Member	Position/Organization	Area of Speciality
L. L. Hench	Professor, Materials Science and Engineering University of Florida	Materials Science
R. J. Charles	Manager, Ceramics Branch, General Electric R & D Center	Materials Science
A. R. Cooper	Professor of Ceramics, Case Western Reserve University	Glass
R. C. Ewing	Chairman, Dept. of Geology, University of New Mexico	Geology, Mineralogy Geochemistry
J. R. Hutchins, III	V.P. & Director, R & D Corning Glass	Glass
D. W. Readey	Professor of Ceramic Engineering, Ohio State University	Ceramics
F. L. VerSnyder	Manager, Materials Technology, United Technologies Research Center, United Technologies Corp.	Metallurgy, Ceramics
S. M. Wiederhorn	Head, Fracture Mechanics Division, National Bureau of Standards	Ceramics

TABLE 17.

RELATIVE RANKING OF CANDIDATE WASTE FORMS BY ALTERNATIVE WASTE FORM PEER REVIEW PANEL (1981)

1) Borosilicate Glass

2) SYNROC

3) High-Silica Glass

4) Tailored Ceramic

5) Coated Sol-Gel Particles

6) FUETAP Concrete

7) Glass Marbles In A Lead Matrix

8) Thermal Spray Coatings

Evaluation and rating techniques employed by the Panel were identical for both reviews. The waste forms were compared on the basis of nine scientific and nine engineering parameters affecting the long-term performance and production of the various forms. Each form was given a numerical rating of 1 to 11 for each parameter considered, and a final group rating for the forms was achieved by averaging the individual scores and through Panel discussions of the available data base. The final results rated each form as either top rank, intermediate rank, or bottom rank in three different categories, (1) Present Scientific Merits or Least Risk for Use Today, (2) Research Priority, and (3) Present and Potential Engineering Practicality. The waste form rankings presented in the reports of the 1979 and 1980 reviews were accompanied by discussions of the relative strengths and weaknesses of the candidate forms and recommendations for future program direction. These reviews and recommendations were instrumental in selecting the seven candidate waste forms considered in the National Program. These seven forms plus two new forms (thermal spray coated glass and ceramic marbles) were assessed in May 1981, the Panel's third and most recent review.

Evaluation Number 3

In the third review[23] of candidate waste forms by the Peer Review Panel in May 1981, the candidate forms assessed were: borosilicate glass, high-silica glass, SYNROC, tailored ceramic, coated sol-gel particles, FUETAP concrete, glass marbles in a lead matrix, thermal spray coated glass marbles, and thermal spray coated ceramic marbles. Although thermal spray coated marbles were evaluated by the Panel, this form was not considered as a potentially viable form in the final waste form evaluation. The precursor of this concept was pyrolytic-carbon and silicon-carbide coated glass marbles, developed at PNL but dropped from consideration because of impractical coating rates and use of inflammable gas mixtures. The thermal spray concept was briefly investigated as an alternative coating process for review by the Panel.

Prior to Panel deliberations, developers presented the most recent waste form information to the Panel. Progress reports describing details of waste form development, characterization, testing procedures, and data for a sufficient comparison of physical properties, chemical durability, and radiation stability and thermal stability were provided to the Panel several weeks before the review. Summary reports, compiling the most recent data obtained from the ongoing research and development efforts for the various waste forms were provided to the Panel at the time of the presentations. These uniform reporting procedures were established to facilitate the comparison of waste form performance parameters. The 1981 review, unlike the two previous evaluations, provided a

consensus ranking of the candidate forms. The ranking was based on relative merits as determined by the Panel using the reports, data, and other information presented or submitted for consideration. The ranking of waste forms as determined by the Peer Review Panel are shown in Table 17.

The Panel reached the following conclusions:

- Borosilicate glass was ranked as the preferred form for geologic disposal of HLW. This conclusion was based on factors such as a relatively simple one-step processing operation, experimental evidence of process insensitivity to waste stream variability, relative insensitivity to radiation, the current routine operation of a full scale remote facility in France, and the equivalent impact resistance of borosilicate glass to the other candidate forms.

- The Panel felt that SYNROC, the second ranked form, was the best characterized and understood of the forms other than borosilicate glass. They concluded that radiation effects on leaching and structural integrity during geological times should be minimal, based on existing data that demonstrate the radiation insensitivity of natural analogs of the various synthetic mineral phases present in SYNROC. Additionally, potential process flexibility relative to densification operations had been demonstrated (i.e. hot pressing, cold pressing, sintering, and hot-isostatic pressing).

- High-silica glass, although offering the process simplicity associated with the production of glass forms and leach resistance equivalent to the crystalline ceramics, was ranked third because of a potentially excessive loss of cesium during densification and because of the very small-scale of forms produced (2-1/2" x 2-1/2") thus far.

- Tailored ceramic was ranked fourth primarily because of a concern about alumina-based magnetoplumbite being the dominant phase for incorporating radionuclides. Little information exists regarding radiation stability of this phase, and no data exist for transmutation effects. The Panel concluded that, although tailored ceramic had promise as a waste form, it was generally more complex and less understood than the vitreous or titanate-based waste forms.

- Coated sol-gel particles ranked fifth. Although extremely low leach rates had been demonstrated for this form, the Panel concluded that the inherent disadvantages of the process and the product outweighed the potential advantages. The waste form is intrinsically one of high surface area and high dispersability. Additionally, the process requires separate handling of cesium

and handling of nine times the volume of liquids presently in waste tanks. Because of the process complexities and the small size of this form, the Panel rated it as relatively unattractive despite its potential for low leach rates.

- FUETAP concrete was ranked sixth by the Panel primarily because leach rates for this form were the highest of any waste form being considered in the National Program. Additionally, the form had 25% porosity and no data existed for radiation effects on mechanical or structural integrity of the form's phase assemblage. The Panel concluded that although this form has the lowest processing temperatures of all the waste forms, the uncertainty regarding long-term stability and leaching is perhaps the greatest.

- Although glass marbles in a lead matrix offer several attractive features such as good thermal conductivity, good mechanical shock resistance, an added barrier for leach resistance, and ease of quality assurance, the Panel ranked the form relatively low. The Panel considered the metal matrix a packaging concept rather than a separate waste form. Additionally, the Panel felt that if the metal barrier was penetrated, "wicking" or penetration of water via unwetted channels between metal and glass would result in leach rates no better than that for glass alone. A high internal surface area and the localized attack could yield higher overall release rates. Therefore, there would be little advantage in using a matrix instead of a can or overpack of the same metal.

- The thermal spray concept involves the use of a plasma gun to apply coatings of metals or ceramics to preformed glass or ceramic pellets or marbles. The major disadvantage is similar to that of the metal matrix, i.e., equivalent leach resistance may be achieved with a metal overpack. No evidence exists that reliable coatings can be applied with a plasma gun, and practical questions concerning the control of excessive coating material in a remotely-operated radioactive facility need to be addressed. Little development work had been performed for the thermal spray approach.

WASTE FORM PRODUCT PERFORMANCE EVALUATION

Introduction and Summary

To provide a quantitative assessment of product performance on a comparable basis for the seven candidate waste forms, an evaluation of several key waste form properties was performed by SRL based on a rating method developed by a DOE Interface Working Group (IWG) on High-Level Waste Form Selection Factors.[24] The rating method used was modeled after the IWG method, with some modifications to account for unavailable characterization data. Comparative data for waste loading, mechanical stability, and leaching were used to evaluate waste form product performance. The final ranking of the seven candidate waste forms and their associated figure-of-merit ratings are shown in Table 18 and are discussed in the following sections.

Product Performance Evaluation Method

The rating method used to quantitatively evaluate the performance of the seven forms is similar to the method developed by the IWG on HLW Form Selection Factors. The IWG, comprised of representatives from DOE waste management programs on HLW, isolation, transportation, and transuranic waste, was established to provide a broad spectrum of expert opinion from which a consensus could be reached on the relative importance among waste form properties, and to develop a method for translating performance data into waste form ratings. A detailed explanation of the method developed by the IWG is described elsewhere.[24]

The IWG identified five categories of waste form properties to be considered in judging the relative merits of candidate waste forms based on product performance. These were leaching (leach rates and solubilities), thermal stability, radiation stability, waste loading, and mechanical stability. These properties were quantified, weighted by relative importance, and organized into a numerical rating scheme representing the three major time periods in the waste disposal system.

1. The Operational period, which includes interim storage, transportation, and handling.

2. The Thermal Pulse period, during which short-lived fission products would still generate significant decay heat. This period was nominally assumed to last about 1000 years after emplacement of the waste in a repository.

3. The Geologic period, after the short-lived radionuclides have decayed.

TABLE 18.

FINAL WASTE FORM PRODUCT PERFORMANCE RANKING AND FIGURE-OF-MERIT SCORES

Waste Form	Figure-of-Merit Score
SYNROC	95
Tailored Ceramic	93
Coated Particles	87[a]
Borosilicate Glass	67
High-Silica Glass	64
Glass Marbles in a Lead Matrix	40[a]
FUETAP Concrete	39

a. Few leaching data available; assumptions were made.

The hierarchy of waste form properties developed by the IWG is shown in Figure 1. Radiation stability, thermal stability, and solubility were not included in this evaluation because of an insufficient comparative data base for these properties. Therefore, the modified hierarchy shown in Figure 2, which contains the waste form properties of leaching, waste loading, and mechanical stability, was used in this evaluation. When this scheme was used with waste form performance data, a "Figure-of-Merit" (FOM) rating was generated for each form. These ratings were then compared, giving a relative ranking of waste form performance.

Figure-of-Merit Score Determination

The comparative "worth" score for a waste form, in each category and each time period, was determined by converting the appropriate performance data to a unitless value by means of a "value function." The procedure assigned a worth score of unity to the best-performing waste form in each category. Scores for the other forms in each category were then less than unity. The worth scores were then multiplied by a weighting factor representing the relative importance of each category. The weighting factors for the three waste form properties considered in this evaluation are shown in Table 19.

The figure-of-merit score for each waste form was obtained by summing the weighted worth scores for all performance categories. The overall procedure can be represented as:

$$FOM = \sum \left(\frac{X_i}{Y_i}\right)^{n_i} * W_i$$

where FOM is the figure-of-merit rating for one waste form; Y_i is the datum (e.g., the measured leach rate) for the best form in the ith category; X_i is the datum for the form being evaluated in the ith category; n_i is an exponent relating the relative worth of any change in the performance measure; and W_i is the relative weight of the ith performance category. If a waste form were "best" in every category, its FOM rating would be 100.

Volumetric waste loading was assigned a value function exponent (n_i) of +0.8 to be representative of the relationship between waste loading and risk of radiation exposure during transportation and handling. Leaching and mechanical stability were assigned an n_i of -0.25 to lessen the impact of technical uncertainties in the experimental data considered in this evaluation. The primary reasons for choosing an exponent of -0.25 were:

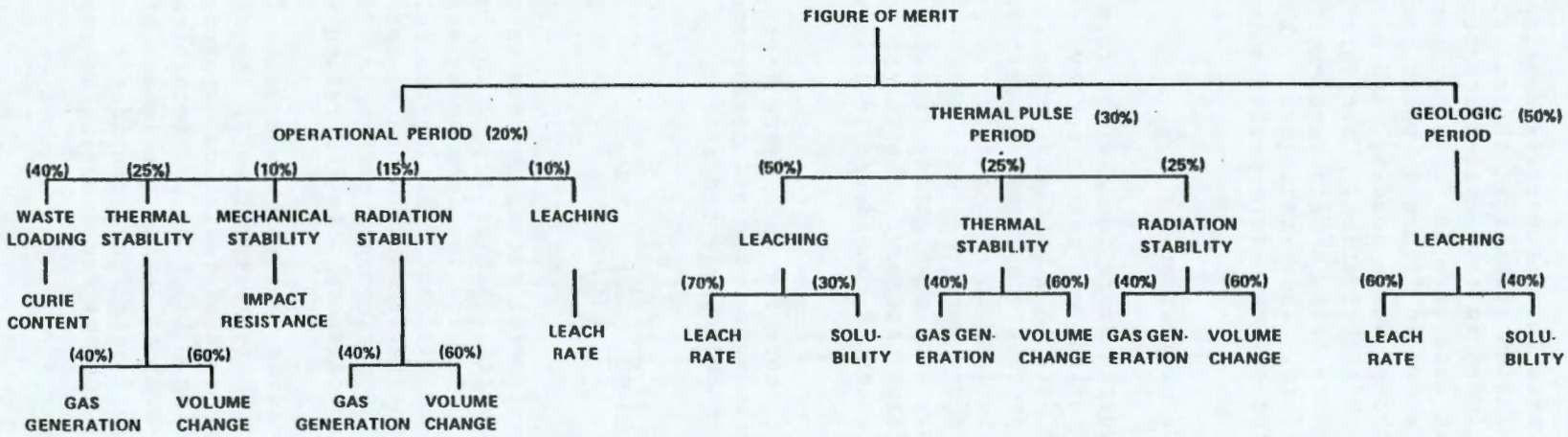

FIGURE 1. Figure-of-Merit Hierarchy for Evaluating Waste Form Product Performance Developed by IWG on HLW Form Selection Factors

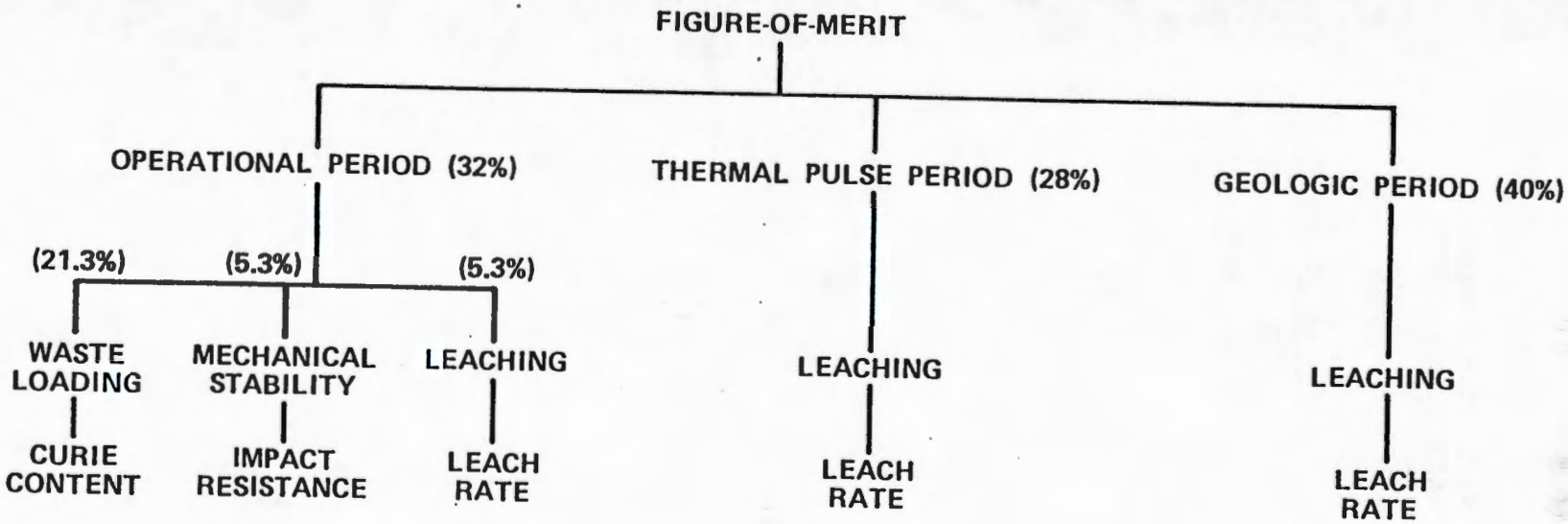

FIGURE 2. Figure-of-Merit Hierarchy Used in the Product Performance Evaluation

TABLE 19.

RELATIVE SIGNIFICANCE OF WASTE FORM PROPERTIES CONSIDERED IN EVALUATING WASTE FORM PRODUCT PERFORMANCE.

Waste Form Property	% Weighting
Leaching	73
Waste Loading	22
Mechanical Stability	5

1. The fundamental leaching mechanisms for all of the candidate forms are not yet known, which prevented meaningful extrapolations of leaching data to repository conditions.

2. Repository risk analyses[25] have generally shown that future health effects are not affected significantly by waste form leach rates in the repository.

3. The variability in leach rate data was about a factor of 2.

4. Actual values for a number of data points were not known because of the variety of detection limits reported for leach rates.

5. Risks for ingestion of radionuclides during a severe handling or transportation accident are greatly mitigated by the shipping cask, which is designed to withstand all credible impacts.

6. The accuracy of the impact resistance data was not known.

Waste Form Characterization Data

To evaluate the relative merits of the seven candidate waste forms, the rating method was applied to comparative data on waste loading, mechanical stability, and leaching. The data were provided by the waste form developers, ANL, the MCC, and SRL. Only data available on or before August 1, 1981, the final date for completion of the waste form comparison, were considered in the product performance evaluation. The significance of the characterization data, and the methods by which these data were obtained are described below.

Waste Loading

Waste loading affects the volume and number of waste forms that must be produced. Lower waste loadings would lead to increased risks in handling and storing a larger number of waste forms, more shipments to the repository, and a larger number of packages to be emplaced in the repository. Waste loading was specified in units of Ci/cm^3 in the final product, as calculated from the weight percent loading in waste forms containing simulated SRP waste. Waste loading data for the seven candidate waste forms are shown in Table 20.

Mechanical Stability

Mechanical stability is related to the risk of public exposure from respirable fines generated by an accidental impact. The data

evaluated were weight percent of fines smaller than 10 micrometers in diameter produced by an impact test at a constant energy-density of 10 Joules/cm^3 (MCC-10 type test).[26] Mechanical stability data are shown in Table 20.

Leaching

Leaching is an important consideration for evaluating the potential performance of candidate waste forms. Resistance to leaching is important because water is the main route for potential dispersion of radionuclides, either following a transportation accident or after emplacement in a repository. Leach rates used in the evaluation were derived from MCC-1, 28 day Static Leach Tests[27] at 40 and 90°C, and the MCC-2 Static, High-Temperature Leach Test[27] at 150°C. It is recognized that the 28 day leach rates are conservative values. They were not meant to be representative of leaching in actual repository environments, nor were they meant to be extrapolated to long-term leaching. However, the MCC-1 and MCC-2 tests were judged to be sufficient for screening the relative potential performance of the various waste forms, and were the only procedures sufficiently well developed to produce the comparable standard data needed for this evaluation.

For evaluating leach rates, certain important radionuclides, leachants, and temperatures were assigned by the IWG to each time period in the FOM hierarchy. These were: for the Operational period, Cs and Sr, in silicate and deionized waters, at 90°C; for the Thermal Pulse period, Cs and Sr, in silicate water and brine, at 90 and 150°C; and for the Geologic period, U, Np, Pu, and Tc, in silicate water and brine, at 40 and 90°C. The leaching temperatures were chosen to bracket all anticipated conditions. Since only simulated waste was incorporated into the waste forms for testing, uranium was used to simulate all actinides for the Geologic period leaching. Cerium and neodymium were also included as actinide simulants, but concentrations of these elements in leachates generally did not reach detection limits. Because of the variety of limits reported by the various laboratories for Ce and Nd, the data could not be normalized to a comparable basis. To compensate for the absent Pu, Np, and Tc data, the uranium data were used to represent 50 percent of leaching in the Geologic period. This weighting assumed that U simulated itself fully, Pu and Np somewhat, and Tc not at all. The rest of the data matrix was completed as specified.

To compare leaching for the seven candidate waste forms, the leach rates were converted to annual fractional release rates using the waste form densities, surface area/mass ratios for full size waste forms in canisters, and a factor of 365 to convert the data to an annual basis. The surface area/mass ratios used in

TABLE 20.

WASTE LOADING AND MECHANICAL STABILITY DATA FOR SEVEN CANDIDATE WASTE FORMS

Waste Form	Waste Loading (Ci/cm^3)	Mechanical Stability (Wt % Fines <10 μm)
Borosilicate Glass	0.36	0.14
SYNROC	0.99	0.16
Tailored Ceramic	0.81	0.06
High-Silica Glass	0.45	0.29
FUETAP Concrete	0.22	0.40
Glass Marbles in a Lead Matrix	0.19[a]	b
Coated Sol-Gel Particles (SYNROC-D)	0.32[c]	b

a. Indicates bulk waste loading with 62% of canister volume as lead.

b. Data unavailable.

c. Indicates bulk waste loading with 38% canister void space.

calculating fractional release rates are shown in Table 21. To combine release rates for different elements within one time period and at the same temperature, the data were weighted by the EPA Maximum Permissible Concentrations of the respective radionuclides in drinking water.[28]

Several laboratories, including the individual developers, the MCC, and SRL, contributed leaching data for the evaluation. No single laboratory contributed an entire data set for all forms. The MCC provided leaching data for four of the forms, SRL tested four of the forms, and each developer tested its own form. Leaching data were often reported as "detection limits", which differed among laboratories because of different analytical methods or equipment. Generally, the leach rate data from the developers, the MCC, and SRL agreed fairly well. However, the variety of detection limits required the establishment of a consistent set of rules for treating the data to determine a final data set for the evaluation. These rules are summarized in Table 22. Tables 23, 24, and 25, list the leach rate data provided by the waste form developers, the MCC, and SRL, respectively. Table 26 shows the consensus leach rate data set derived from Tables 23-25, by using the rules specified in Table 22.

Application of the Evaluation Method

Application of the evaluation method to rate the seven candidate waste forms based on the product performance data required making certain assumptions. The assumptions, discussed briefly below, were made to 1) compare leach rate data reported as detection limits, and 2) allow for the treatment of waste forms not specifically adaptable to the rating method. The sensitivity of the product performance results to uncertainties in the characterization data, and to various assumptions made to evaluate the data, are discussed in Appendix A. The product performance ranking of the waste forms was relatively insensitive to assumptions used in the evaluation procedure and to uncertainties in characterization data. Any sensitivities that did occur were moderated when the product performance and processability ratings were considered together.

Leach Rate Detection Limits

When leach rate data for the different waste forms were compared, detection limits became an important factor. Previously described treatments of the data were used to compare real values and unequal limits. Additionally, several categories of leaching data, such as brine leaching at 40°C, were dominated by the

TABLE 21.

SURFACE AREA/MASS RATIOS FOR THE SEVEN CANDIDATE WASTE FORMS[a]

Waste Form	Surface Area/Mass (cm^2/g)
Borosilicate Glass	0.029
SYNROC	0.018
Tailored Ceramic	0.018
High-Silica Glass	0.026
FUETAP Concrete	0.036
Glass Marbles in a Lead Matrix	0.51[b]
Coated Sol-Gel Particles	1.03[c]

a. In order to determine SA/m ratios for borosilicate glass, SYNROC, tailored ceramic, high-silica glass, and FUETAP concrete, the geometric surface area of a monolith 2 ft in diameter by 8 ft high within a 2 ft by 10 ft canister was assumed. Increased surface area due to cracking was not considered. Actually, surface area will depend on the extent of cracking, and if the forms are a single monolith or several smaller monoliths stacked in a single canister. Mass was calculated as the waste form density times the volume of the monolith.

b. It was assumed that glass occupied 62%, and lead 38% of the volume of a 2 ft diameter by 10 ft canister 80% full. A SA/m was calculated using the geometric surface area of a 2 ft by 8 ft monolith and the total mass of glass and lead. This value was averaged with a SA/m calculated from the geometric surface area and mass of the glass marbles only. The average of the two SA/m ratios was used to represent the SA/m for the cast metal matrix form.

c. It was assumed that 38% of the volume of a 2 ft diameter by 10 ft canister, 80% full of coated particles, was interstitial void space. The total surface area was calculated as the number of coated particles (1.5×10^8) in the canister, times the average surface area for a single coated particle (1.2×10^{-2} cm^2). The total mass was calculated as 1.5×10^8 times the average mass of a single coated particle ($1.2 \times 10^{-2}g$).

TABLE 22.

RULES FOR TREATING LEACH RATE DATA TO DETERMINE CONSENSUS DATA MATRIX

Each entry in the consensus data matrix was a single value, derived from multiple data sources that were combined by the following treatments:

1. All leach rate data reported as real values (non-limits) were averaged.

2. When all data reported were detection limits, the lowest limit was used.

3. When comparing a detection limit and a non-limit (real) value: If the detection limit was higher, the real value was used.[a]

4. When comparing a detection limit and a non-limit (real) value: If the limit was equal to the real value, the real value was used and not recorded as a detection limit.

5. If only one data point was reported, that value was used.

6. SRL data for non-representative tailored ceramic and SYNROC forms were not used.

7. Fourteen-day data reported by the MCC were used to check for agreement, but were not included in the final data set.

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a. This treatment was applicable in all cases except one. Strontium leach rates for borosilicate glass at 150°C in brine were reported as <.006 and 2.60. For this case the two values were averaged and reported as a limit.

TABLE 23.

LEACH RATE DATA OBTAINED FROM THE WASTE FORM DEVELOPERS FOR MCC-1 AND MCC-2 STATIC LEACH TESTS

Conditions/ Element		Leach Rate ($g/m^2.d$) Waste Form[a]						
		BSG	SYN	TC	HSG	FUE	Pb-M	CP
Deionized H_2O								
90°C	Cs	0.58	0.79	4.50	<.10	48.	0.13	-
	Sr	<.001	0.38	0.0011	0.157	0.27	<.01	-
Silicate H_2O								
40°C	U	0.036	<.0185	0.00093	<.02	0.007	-	<.0001[b]
90°C	Cs	0.49	0.54	2.25	<.20	37.	<.04	-
	Sr	<.001	0.099	<.00036	0.0425	0.30	<.01	-
	U	0.44	<.0185	0.0021	0.121	0.02	-	0.00015[b]
150°C	Cs	1.71	0.74	8.14	1.02	-	<.04	-
	Sr	0.006	0.493	<.00036	0.239	-	<.10	-
Brine Solution								
40°C	U	<.71	<.0185	<.0011	0.038	0.06	-	-
90°C	Cs	0.35	-	5.46	<.20	53.	-	-
	Sr	<.001	<.71	<.00036	0.546	23.	<.10	-
	U	<.71	<.0185	<.0011	0.0028	0.06	-	-
150°C	Cs	2.65	1.96	5.46	0.654	-	<3.80	-
	Sr	2.60	1.53	-	1.43	-	0.15	-

a. Waste Form Abbreviations: BSG: borosilicate glass; SYN: SYNROC-D; TC: tailored ceramic; HSG: high-silica glass; FUE: FUETAP concrete; Pb-M: glass marbles in a lead matrix; CP: coated sol-gel particles.

b. Indicates 14 day data

TABLE 24.

LEACH RATE DATA OBTAINED FROM THE MATERIALS CHARACTERIZATION CENTER FOR MCC-1 AND MCC-2 STATIC LEACH TESTS

Conditions/ Element		Leach Rate ($g/m^2.d$) Waste Form						
		BSG	SYN	TC	HSG	FUE	Pb-M	CP
Deionized H_2O								
90°C	Cs	1.23	0.70	-	-	-	-	-
	Sr	<.006	0.28	-	-	-	-	-
Silicate H_2O								
40°C	U	0.016[a]	0.00013[a]	0.00066[a]	0.052a	-	-	-
90°C	Cs	0.94	0.22	0.13[a]	0.20[a]	-	-	-
	Sr	<.006	0.079	-	0.16[a]	-	-	-
	U	0.18	0.00021	0.0023[a]	0.30[a]	-	-	-
150°C	Cs	2.85	-	-	-	-	-	-
	Sr	<.006	-	-	-	-	-	-
Brine Solution								
40°C	U	-	-	-	-	-	-	-
90°C	Cs	<1.3	<.10	-	-	-	-	-
	Sr	<.33	<.20	-	-	-	-	-
	U	0.011	0.0005	-	-	-	-	-
150°C	Cs	1.90	<.24[a]	<.24[a]	<.24[a]	-	-	-
	Sr	<.006	2.21[a]	-	3.90[a]	-	-	-

a. Indicates 14-day data.

TABLE 25.

LEACH RATE DATA OBTAINED FROM SAVANNAH RIVER LABORATORY COMPARATIVE LEACH TESTING PROGRAM

Conditions/ Element		Leach Rate ($g/m^2.d$) Waste Form						
		BSG	SYN	TC	HSG	FUE	Pb-M	CP
Deionized H_2O								
90°C	Cs	1.54	0.49	5.09	0.028	-	-	-
Silicate H_2O								
90°C	Cs	0.76	0.39	1.44	0.121	-	-	-
	U	0.30	0.0016	0.013	0.102	-	-	-

TABLE 26.

CONSENSUS LEACH RATE DATA FOR THE SEVEN CANDIDATE WASTE FORMS.

CONDITIONS/ ELEMENT		LEACH RATE ($g/m^2.d$) WASTE FORM						
		BSG	SYN	TC	HSG	FUE	Pb-M	CP
Deionized H_2O								
90°C	Cs	1.12	0.75	4.50	0.028	48.	0.13	-
	Sr	<.001	0.33	0.0011	0.157	0.27	<.01	-
Silicate H_2O								
40°C	U	0.036	<.0185	0.00093	<.02	0.007	-	-
90°C	Cs	0.73	0.38	2.25	0.121	37.	<.04	-
	Sr	<.001	0.089	<.00036	0.0425	0.30	<.01	-
	U	0.31	0.00021	0.0021	0.111	0.02	-	-
150°C	Cs	2.28	0.740	8.14	1.02	-	<.04	-
	Sr	0.006	0.493	<.00036	0.239	-	<.01	-
Brine Solution								
40°C	U	<.71	<.0185	<.0011	0.038	0.06	-	-
90°C	Cs	0.35	<.10	5.46	<.20	53.	-	-
	Sr	<.001	<.20	<.00036	0.546	23.	<.10	-
	U	0.011	0.0005	<.0018	0.0028	0.06	-	-
150°C	Cs	2.28	1.96	5.64	0.654	-	<3.8	-
	Sr	<1.33	1.53	<.039	1.43	-	0.15	-

difficulty of analyzing solutions of high ionic strengths. Data taken at 90°C, however, were often sufficiently differentiated to allow the calculation of leaching values at 40°C that were better than those available from direct tests. Assumptions used to compare these data were:

- When comparing data for a specific factor, if several different detection limits were reported for different waste forms, all data (real values or detection limits) lower than the highest limit reported were adjusted to that limit. Real, non-limit values larger than the highest limit were not changed. This method allowed the forms to be compared on a uniform basis, and did not penalize a developer with less sensitive analytical tools. The method is technically valid, because the highest limits (e.g., "less than 0.1 $g/m^2.d$") envelop smaller limits or values (e.g., "less than 0.01 $g/m^2.d$", or "0.05 $g/m^2.d$").

- When detection limits reported at 40°C were higher than actual data or detection limits for the same waste form at 90°C in the same leachant, the 90°C data replaced the 40°C limits. This approach assumed that a waste form would not leach faster at a lower temperature, under otherwise identical conditions. Only limits, not actual values, were changed.

The final matrix of leaching data generated under these assumptions and considered in the product performance evaluation is shown in Table 27.

Special Waste Forms

The coated particle and metal matrix waste forms are composites; they include additional, time-dependent barriers as integral parts of their structures. Therefore, these forms could not be evaluated on an equal basis with the other candidate waste forms. The IWG concluded that "waste form specimens that have been exposed to the relevant thermal and radiation damage simulations prior to leaching are the most representative";[24] none of the waste forms considered in this evaluation received such treatments. However, previous leaching conditions that might be experienced by the coated particle and metal matrix forms during the Thermal Pulse and Geologic periods could significantly affect the integrity of particle coatings or of metallic networks. The amount of leachable surface area from failed particle coatings (or exposed glass marbles) would depend on the detailed histories of the waste forms, which could not be simulated in the short-term MCC tests.

Few performance data were available for the coated particle and metal matrix waste forms. Comparable data were unavailable on

TABLE 27.

FINAL LEACH RATE DATA MATRIX USED IN PRODUCT PERFORMANCE EVALUATION

Conditions/ Element		Leach Rate ($g/m^2.d$) Waste Form						
		BSG	SYN	TC	HSG	FUE	Pb-M	CP[a]
Deionized H_2O								
90°C	Cs	1.12	0.75	4.50	0.028	48.	0.13	-
	Sr	<0.001	0.33	0.0011	0.157	0.27	0.001[b]	-
Silicate H_2O								
40°C	U	0.036	<0.02[c]	<0.02[c]	<0.02	<0.02[c]	0.036[b]	-
90°C	Cs	0.73	0.38	2.25	0.121	37.	<0.04	-
	Sr	<0.001	0.089	<0.001[c]	0.043	0.30	0.001[b]	-
	U	0.31	0.00021	0.0021	0.111	0.02	0.31[b]	-
150°C	Cs	2.28	0.740	8.14	1.02	37.[d]	0.04	-
	Sr	0.006	0.493	<0.00036	0.239	0.30[d]	0.01	-
Brine Solution								
40°C	U	0.011[e]	<0.0011[e,c]	<0.0011	0.038	0.06	0.011[b]	-
90°C	Cs	0.35	0.20[c]	5.46	<0.20	53.	0.35[b]	-
	Sr	<0.20[c]	<0.20	<0.20[c]	0.546	23.	<0.20[c]	-
	U	0.011	<0.0018[c]	<0.0018	0.0028	0.06	0.011[b]	-
150°C	Cs	2.28	1.96	5.64	0.654	53.[d]	2.28[b]	-
	Sr	1.38	1.53	<0.039	1.43	23.[d]	0.15	-

a. Set equal to best leach rate of other forms in all categories.

b. Set equal to borosilicate glass.

c. Lower value or limit raised to another form's detection limit.

d. Value assigned equal to 90°C data for consideration in evaluation.

e. 90°C value.

mechanical stability of either form, uranium leaching of the metal matrix form, and all leaching of the coated particle form. Coated particle waste forms were prepared with simulated waste for comparitive leach testing, but this information was not available at the time of the evaluation. To address these data absences, several assumptions were made so that these forms could be included in the evaluation.

Normalized fractional release rates for coated particles in each time period were set equal to the best rates measured for any other waste form. This treatment was based on preliminary data indicating potentially very low leach rates for the coated particle form.[29] Where actual data were available for glass marbles in a metal matrix, these data were used. If data for the glass marble form were unavailable, borosilicate glass leach rates were used, assuming that glass marbles in a lead matrix would have leach rates no greater than those of a glass monolith. For mechanical stability, both of the composite forms were assigned performance measures equal to the best of the other forms. It was assumed that in an impact accident scenario, the presence of the lead matrix or the void spaces between coated particles would provide buffering against any significant generation of fines from these forms.

Results

The final ranking of the seven candidate waste forms and the associated figure-of-merit scores resulting from the product performance evaluation are shown in Table 18. The seven forms can be grouped into three categories: 1) the two ceramic forms and coated particles rated highest; 2) the borosilicate glass and high-silica glass forms have intermediate ratings; and 3) the metal matrix form and FUETAP concrete have the lowest ratings. The two ceramic forms, SYNROC and tailored ceramic, ranked highest because of the high waste loadings and low uranium leach rates reported for them. The coated particle waste form had a slightly lower, but indistinguishable rating. Although this form was assigned scores equal to the best of the other candidate forms for most of the data considered, its overall score and position were a result of a relatively low waste loading. While the waste loading of a single particle is relatively high (70 wt %), the bulk waste loading is significantly reduced after considering coating volumes and an assumed 38% canister void space.

The glass forms, borosilicate glass and high-silica glass, had comparable intermediate ratings, with a slight edge going to borosilicate glass. Both of these forms demonstrated moderate waste loadings and good Cs and Sr leach rates, which on the average were slightly better than those for the ceramic forms. However,

their uranium leach rates were somewhat higher than for the crystalline ceramic forms.

The metal matrix and concrete forms ranked in the lowest category. These forms had the lowest waste loading values of any of the waste forms considered. Additionally, concrete had the poorest impact resistance and the highest overall leach rates. Although the metal matrix form had relatively low leach rates, the moderately high surface area/mass ratio for the form had an effect of increasing the annual fractional release rate.

Discussion and Conclusions

The waste form product performance ratings reflect only an approximate relative indication of their performance as waste forms. As shown in Table 18, there is a wide margin of difference between the highest and lowest rated waste forms, which allows a reasonably confident distinction to be made between them. This conclusion is supported by results of the sensitivity analysis discussed in Appendix A.

Discrimination is less clear between waste forms in the high and intermediate rating categories (viz. ceramics versus borosilicate glass), for several reasons. Relative leach rates for ceramic versus glass forms are mixed for the three elements evaluated (U, Cs, and Sr). Ceramic forms rated highest because of their low U leach rates, but the glass forms rated slightly better for Cs and Sr. Additional uncertainties include errors in the data, the variability in detection limits reported for leaching, and uncertainties related to extrapolation from the reported leach test conditions for very short leaching periods to repository conditions for geologic time periods. As an example, of the latter, borosilicate glass tends to build a protective oxide layer, which reduces its leach rate for long (>28 day) leaching times. Possibly this phenomenon could reduce the observed difference in uranium leachabilities between the ceramic and glass forms.

In comparing waste forms within each of the three rating categories, the ratings are too close to permit any meaningful discrimination to be made based on product performance alone. There is virtually no difference in performance between SYNROC and tailored ceramic, or between borosilicate glass and high-silica glass, based on the data base used.

The assignment of worth scores to various levels of product performance (i.e., the nature of the "value function" to be used) depends heavily on the performance of the entire waste disposal system, not just the waste form. Design of other barriers to radionuclide release in a repository, the behavior of the rock

overlying the repository, potential precipitation reactions, dilution of radionuclides in leaching groundwaters, and any time delays before waste elements could be transported to the earth's biosphere, were not considered in this evaluation. Expected time delays would allow major hazardous radionuclides, such as short-lived fission products, to decay to an insignificant level before they could be released.

As knowledge of the long-term behavior of a waste repository and the design of the disposal system progresses, a better understanding of the worth of different levels of product performance will develop. Some threshold level of waste form performance, improvement of which would not significantly affect the radiological protection of future human populations, would be appropriate. Such judgments were not made in this evaluation.

WASTE FORM PROCESSABILITY ANALYSIS

Introduction and Summary

To provide a quantitative assessment of the processes required for producing the seven candidate waste forms, a processability analysis was conducted by the Du Pont Engineering Department for the Savannah River Laboratory (SRL). The purpose of the study was to evaluate the relative feasibility of processing the candidate forms in a shielded and remotely operated Defense Waste Processing Facility (DWPF). This assessment was considered equal in importance to the product performance evaluation in the screening of the seven candidate forms. Results of the processability analysis and the product performance evaluation were combined to obtain a single rating of the seven forms.

The processability analysis involved: the definition of individual waste form processes by the developers; development of flowsheets, equipment concepts and conceptual designs by the Engineering Department; and the quantitative rating of the processes, also by the Engineering Department. Process factors considered in the analysis included complexity, reliability, resource requirements, safety, and quality control.

The processes evaluated and the methodology and results of the analysis are described below. Merit ratings of the processes are summarized in Table 28. The reference process, borosilicate glass, was rated as the best (simplest) process, followed closely by FUETAP concrete. The other waste form processes in order of increasing complexity were: glass marbles in a lead matrix, high-silica glass, crystalline ceramics (SYNROC and tailored ceramic), and coated sol-gel particles. Details of the evaluation are documented in a report published by the Savannah River Laboratory.[30]

Ground Rules

Several ground rules were set by SRL as bases for the processability analysis. The principal ground rules were:

1. Processes should be for the immobilization of SRP waste, including both sludge and cesium concentrate from the supernate.

TABLE 28.

PROCESSABILITY ANALYSIS FINAL FIGURE-OF-MERIT RATINGS

Process	Figure-of-Merit
Borosilicate Glass	83
FUETAP Concrete	77
Glass Marbles in a Lead Matrix	58
High-Silica Glass	51
Crystalline Ceramics	42
Coated Particles	32

2. Conceptual designs should include only Stage 1 of the proposed Defense Waste Processing Facility.*

3. Conceptual designs should incorporate Du Pont operating and maintenance philosophy for nuclear material processing facilities (e.g., completely remote operation and maintenance and no explosive gas mixtures allowed).

4. All process steps must have defined, but not necessarily developed equipment concepts.

Waste Form Processes Evaluated

Six candidate waste form processes were evaluated (Table 29). Initial process descriptions were provided by the waste form developers. Subsequently, in collaboration with the developers and SRL, process flowsheets, material balances, equipment definitions, and conceptual facility layouts were developed by the Engineering Department for each candidate process. Abridged descriptions of the processes are given below.

Borosilicate Glass

A slurry of washed sludge from the tank farm is pumped to a sludge receipt and adjustment tank (SRAT) where it is adjusted with formic acid and boiled under reflux to reduce the sludge oxidation state and reduce mercury to the liquid state. Liquid mercury settles and collects in a sump, and is periodically transferred from the sump to mercury recovery. The treated sludge slurry is transferred to a slurry mix evaporator (SME) where it is blended with a water slurry of fresh glass frit and spent frit generated in canister decontamination. Strontium concentrate,** cesium concentrate adsorbed on zeolite, recycled solids, and waste sand from the Stage 2 facility are also mixed with sludge and frit in

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* Present plans for the DWPF call for the construction of two facilities built in sequential stages to reduce the initial capital investment. The Stage 1 facility is the waste solidification facility which will initially immobilize the sludge component of SRP wastes. In the Stage 2 facility, the radionuclides (primarily cesium) in the dissolved or supernate portion of the waste will be concentrated and then transferred to the Stage 1 facility for solidification with the sludge.

** Almost all of the strontium in SRP HLW is precipitated in the sludge fraction. However, a very small amount of strontium concentrate is also generated in decontaminating the SRP supernate waste in Stage 2.

TABLE 29.

CANDIDATE WASTE FORM PROCESSES EVALUATED

Waste Form	Process
Borosilicate Glass	Slurry Fed Glass Melter
High-Silica Glass	Rising-Level In-Can Sintering
SYNROC	Hot Isostatic Pressing
Tailored Ceramic	Hot Isostatic Pressing
FUETAP Concrete	Formed Under Elevated Temperatures and Pressures
Glass Marbles in a Lead Matrix	Slurry Fed Glass Melter; Marble Machine; Lead Matrix
Coated Particles	Sol-Gel Sphere Formation with CVD Coating of PyC and SiC

the SME.* The composite slurry is then concentrated to about 40 wt% solids by evaporating excess water.

The adjusted slurry is continuously fed from feed tanks to a joule-heated melter operating at 1150° ± 25°C to form a homogeneous molten glass. After melting and homogenization, molten glass is poured into a 2 ft dia by 10 ft tall canister and allowed to cool. The filled canister is sealed by welding a plug into the canister throat using an upset resistance welder. The canister is then decontaminated and transferred to interim storage.

High-Silica Glass

Sludge from the tank farm is received as a slurry and treated with formic acid in the sludge receipt and adjustment tank (SRAT) to reduce the overall sludge oxidation state and precipitate metallic mercury. Liquid mercury after settling is transferred periodically to a mercury evaporator. Treated sludge is transferred to the slurry mix evaporator (SME) where it is blended with strontium concentrate, cesium concentrate adsorbed on porous high-silica glass frit, waste sand from Stage 2, glass frit generated in canister decontamination, and recycled solids. In the SME, the solids are concentrated to 40 wt %.

The slurry is then calcined in a spray calciner at 650°C. The calcine powder is transferred pneumatically to calcine-frit blenders via a fluid energy mill which reduces particle size to less than 50 microns. Additional frit is added to the calcine and thoroughly mixed in the calcine-frit blenders. The mixture is then transferred to a feed bin prior to the in-can fusing operation.

Fusing of the glass frit and waste particles is accomplished by a rising-level sintering procedure within the canister. Before charging the in-can sintering furnace, the feed bin and the canister are put under a moderate vacuum of 10-20 torr, and the canister is inductively heated to about 1200°C. The calcine-frit blend is then fed to the canister and radiantly heated during

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* Since the completion of the processability analysis, the reference borosilicate process has been changed to a simpler, more compact ion exchange process, in which cesium is transferred from the Stage 2 facility to the SME in a formate solution.

freefall to achieve a temperature of at least 800°C, which causes the internal pores of the cesium loaded frit to collapse and trap the cesium. Glass frit and waste particles at the bottom of the canister fuse together at about 1100°C - 1150°C. This procedure continues until the canister is filled with a fused mixture of waste particles and high-silica glass. Considerable homogenization occurs during sintering at 1150°C; however, waste particles remain as discrete entities in the high-silica glass matrix (as verified by Scanning Electron Microscopy).

Filled canisters are cooled, sealed with a plug weld, and decontaminated for interim storage.

Crystalline Ceramics - SYNROC and Tailored Ceramic

Sludge from the tank farm is received in a sludge receipt tank and transferred to a slurry mix evaporator (SME). Sludge, waste sand from Stage 2, cesium-loaded zeolite, canister decontamination slurry, and recycled solids are combined and the mixture concentrated to 40 wt % solids by removing excess water in the SME. The resulting slurry is batch loaded into ball mills for approximately 6 hours of milling to achieve a particle size distribution of 95% less than 10 microns required for the production of the ceramic waste form.

The milled slurry is transferred in batches to a spray calciner operating at 650°C. A dehydrated powder containing intimately mixed oxides of waste components and ceramic additives exits the calciner and is pneumatically transferred via a fluid energy mill into a mixer/blender. Iron powder is added to the calcine in the mixer/blender for control of the oxidation state of the powder. The calcine is then loaded in a canister via a batch bin and intermittently tamped during filling to achieve 50% of theoretical density.

The filled canister is evacuated to 10 torr, sealed, and preheated to a centerline temperature of 800°C. The preheated canister is then transferred to a hot isostatic press (HIP). After closure, the HIP is pressurized with argon to 15,000 psi. The temperature is increased until the canister centerline reaches 1150°C. Under these conditions, the canister volume is reduced by 50%. Following consolidation, the pressure is reduced to atmospheric and the canister is allowed to cool. The canister is then decontaminated and sent to interim storage.

Mercury removal is accomplished in the off-gas scrubber system, with a recovery and purification process similar to that of the reference borosilicate glass process.

FUETAP Concrete

A slurry of washed sludge from the tank farm is transferred to a steam heated slurry mix tank (SMT). In the SMT, strontium concentrate, cesium-loaded zeolite, waste sand from Stage 2, and recycled solids are added to the sludge slurry. The contents of the SMT are blended and pumped to a spray calciner operating at 650°C.

Periodically, dry calcine is blended in-line with cement, fly ash, and sand, and sent to a dry batch bin located directly over a wet batch cement mixer. Measured amounts of water and water reducer are charged to the wet batch mixer, and the dry batch is added over a two hour period to form a wet batch.

Once the concentration of solids in the wet batch mixer is such that the batch will solidify, a discharge chute is positioned over a canister, and the wet batch is discharged into the canister. After the concrete has solidified (4-10 hours), the canister is loaded into an induction heated curing oven. The oven cycle, lasting 30 hours, is staged to accomplish curing and dewatering. Curing is performed unvented at 100°C with one atmosphere of steam pressure developing in the canister. Dewatering at 250°C under slight vacuum removes approximately 89% of all water in the concrete. Once the oven cycle is complete, final closure is accomplished by upset resistance welding a plug into the canister throat. The canister is then decontaminated and sent to interim storage.

Mercury removal is accomplished in the off-gas scrubber system with a recovery and purification process similar to that of the reference borosilicate glass process.

Glass Marbles in a Lead Matrix

The process steps required to produce the glass melt that feeds the marble-making machine are exactly the same as those required to produce borosilicate glass.

Following melting and homogenization, molten glass exits the melter into a machine that produces 1.3 cm diameter marbles. Marbles are pneumatically transferred through a batch bin and into the canister. After filling, the marble-loaded canister is transferred to an induction furnace where lead matrix material is added in the form of shot. The canister is designed to contain the glass marbles such that the lead matrix completely encloses the glass marbles. During the matrix filling operation, the induction furnace provides the heat to melt the lead. To avoid shrinkage and insure that the canister annulus and all inter-marble

spaces are completely filled, the induction furnace provides zone heating to facilitate lead solidification from the bottom upward. Near the end of the solidification cycle, additional lead is added to fill the shrinkage cavity. The canister is then sealed with a plug weld, decontaminated, and sent to interim storage.

Coated Sol-Gel Particles

A slurry of washed sludge is received from the tank farm and adjusted by formic acid addition to reduce the oxidation state of the waste and preciptate liquid mercury. Mercury is then separated and sent to mercury recovery. Strontium concentrate is received in a vessel where Na-EDTA complexes are oxidized by ozonolysis. Waste sand from Stage 2 and recycle solids pass through a grinder and are sent to a pump tank. The sludge slurry, together with the strontium from the oxidation vessel and the waste sand, are sent to a nitric acid digester and combined with water and zirconium nitrate.

After screening, the nitric acid feed is combined with 1.5 pounds of urea per pound of sludge solids in the feed to form a broth. This broth is then refrigerated to 0°C. Hexamethylenetetramine (HMTA) is mixed with the broth and fed to the spray heads of the gel forming column. The U-shaped gel forming column allows the gel to fall freely through an organic suspending liquid of trichloroethylene and 2-ethylhexanol which circulates in the column at 55°C. The particles formed are allowed to age in the organic forming fluid for about one hour and then sent to a gel washing step.

Washed gel spheres are transfered to a fluid-bed dryer where they are suspended with hot air until small enough to be blown to a hold tank by the fluidizing air. Dried gel spheres are then transferred to sintering furnaces and sintered at 900°C in a hydrogen-nitrogen atmosphere to produce small spherical ceramic particles suitable for coating.

Cesium removed in the gel washing step and cesium eluate from Stage 2 are combined and fed through parallel zeolite columns for removal of the cesium. Periodically, the contents of these columns are sintered in air at 600°C to close the pores of the zeolite, fixing the cesium in the zeolite particles. These zeolite particles are then suitable for coating.

The sintered gel spheres and sintered zeolite particles are then transferred to coaters for appplication of three different coatings. The first coating is a low-density, silicon carbide coating applied by fluidizing the particles in methylsilane and nitrogen at 1000°C. The temperature is reduced to 900°C and a

second, but high-density, silicon carbide coating is applied. The final coating is pyrolytic carbon applied by fluidizing the particles in propylene and nitrogen at 1200°C.

The coated spheres and particles are then loaded into a canister while being sprayed with an inorganic cement to fix the particles in the canister. The canister is baked at approximately 200°C to expel water from the cement. The canister is then sealed with a plug weld, decontaminated, and sent to interim storage.

Rating Method

To assess the relative merits of the waste form processes, twenty-one processability criteria in four major categories were defined and weighted relative to their overall importance. Design data from the process flow sheets, equipment definitions, and facility layouts developed by the Engineering Department were used to rate each process against these criteria. The four major criteria categories, complexity/reliability, resource requirements, safety, and quality control were weighted 40, 25, 20, and 15 percent, respectively. Units of measure for all of the criteria are defined in Table 30. A figure-of-merit rating method, similar to and compatible with the product performance evaluation method, was used to rate each process for all 21 criteria. The merit rating (R) of each process was calculated by taking a weighted sum of normalized value functions:

$$R = \sum_{i=1}^{21} W_i \, (Y_i/X_i),$$

Where W_i is the weight of the ith criterion or factor, (Y_i/X_i) is the value function for the ith processability factor, X_i is the value of the ith factor for the process being considered and Y_i is the value of the ith factor for the process having the best value for that factor.

The criteria were quantitative in all cases. For all criteria, a value function having the inverse relationship $(X/Y)^{-1}$ was used to convert the data to a common scale. A waste form process receiving the highest value for each criterion would receive a process merit rating of 100.

Results and Conclusions

The raw scores or process values and the weighted, normalized scores by category are shown in Tables 31 and 32, respectively.

TABLE 30.

WASTE FORM PROCESSABILITY ANALYSIS CRITERIA

Factor	Relative Weight	Unit of Measure
A. Complexity-Reliability (40%)		
1. Critical control parameters	10	Count of control points required to maintain product quality or operability
2. Process cell requirements	8	Square feet - Length of process cells x 60 ft standard width
3. Process steps	6	Count of steps accomplishing a function
4. Equipment pieces at high temperature (>350°C) or high pressure (>150 psi)	4	Count of major equipment pieces above temperature or pressure. Pieces are counted twice if both temperature and pressure are exceeded.
5. Unusual service facilities	4	Count of equivalent small facilities (one large facility equals three small facilities).
6. Recycle loops	2	Count of process flows returning to preceding steps
7. Equipment pieces in covered cells	2	Count
8. Chemical additions through walls	2	Count
9. Dry radioactive materials transfer steps	2	Count
	40	
B. Personnel Safety (20%)		
1. Radioactive high maintenance equipment pieces	10	Count of equipment pieces in corrosive, erosive, high temperature, high pressure environment.
2. Process steps at high temperature or pressure	5	Count of steps at high temperature (>350°C) or pressure (>150 psi). Pieces are counted twice if both temperature and pressure are exceeded.
3. Other hazardous materials	5	Count of hazardous materials used, each factored by number of hazards (toxic, chronic, flammable/explosive)
	20	

TABLE 30, Contd

Factor	Relative Weight	Unit of Measure
C. Quality Control and Assurance (15%)		
1. Product tolerance to process variations	7.5	Count of critical control points for Product Quality weighted for ease of control. One being easy, two being moderate, and three being difficult.
2. Dry particle processing steps	3	Count
3. Steps to prepare and test sample	3	Count steps for quality assurance samples only
4. QC sampling points	1.5	Count quality control sampling points
	15	
D. Resource Requirements (25%)		
1. Capital cost	7.5	Square feet - (length of process cells + 243 ft) x 132 ft standard width
2. Development items	7.5	Count of equipment pieces or control concepts needing remote operation development
3. Raw materials	2.5	Annual consumption x price = $/yr
4. Decontamination and disposal	3.75	Equivalent number of building modules + 5x those in category B-1
5. Lag storage	3.75	Cubic feet space for container storage - 1 year
	25	

TABLE 31.

RAW DATA SCORES FOR PROCESSABILITY ANALYSIS CRITERIA

Process Factor	Candidate Waste Forms					
	Borosilicate Glass	Glass Marbles in Lead Matrix	High-Silica Glass	FUETAP Concrete	Crystalline Ceramics	Coated Particles
A. Complexity-Reliability (40%)						
1. Critical control parameters	4	7	7	4	11	12
2. Process cell requirements M ft^2	11.2	13.0	14.9	17.2	23.4	33.1
3. Process steps	7	10	10	11	10	27
4. Equipment pieces at high temperature (>350°C) or high pressure (>150 psi)	2	4	5	1	7	8
5. Unusual service facilities	6	8	11	6	9	16
6. Recycle loops	1	2	2	4	3	10
7. Equipment pieces in covered cells	8	11	13	13	39	40
8. Chemical additions through walls	7	8	7	6	12	18
9. Dry radioactive materials transfer steps	1	5	10	3	5	19
B. Personnel Safty (20%)						
1. Radioactive high maintenance equipment pieces	6	8	12	5	20	18
2. Process steps at high temperature or pressure	2	3	2	1	4	4
3. Other hazardous materials	8	8	7	7	10	21

TABLE 31, Contd

Process Factor	Candidate Waste Forms					
	Borosilicate Glass	Glass Marbles in Lead Matrix	High-Silica Glass	FUETAP Concrete	Crystalline Ceramics	Coated Particles
C. Quality Control/Assurance (15%)						
1. Product tolerance to process variations	4	7	10	2	10	8
2. Dry particle processing steps	1	3	3	2	3	5
3. Steps to prepare and test sample	2	1	3	4	5	1
4. QA sampling points	4	4	5	3	6	13
D. Resource Requirements (25%)						
1. Capital cost building[a] M ft^2	56.8	60.6	64.8	70.0	83.6	104.8
2. Development items	2	7	7	4	12	18
3. Raw materials M $/yr	1947	6629	8258	2897	1194	2018
4. Decontamination and disposal	56	71	96	67	156	171
5. Lag storage M ft^3	14.5	28.9	15.5	25.7	2.9	5.7

a. Capital cost is a function of fixed cost plus cost relating to building size, with building size being the major contributing factor to overall facility cost.

TABLE 32.

PROCESSABILITY ANALYSIS FIGURE-OF-MERIT SCORES FOR THE MAJOR PROCESSABILITY CRITERIA CATEGORIES

	Candidate Waste Forms					
Major Processability Category	Borosilicate Glass	Glass Marbles in Lead Matrix	High-Silica Glass	FUETAP Concrete	Crystalline Ceramics	Coated Particles
Complexity-Reliability	38	26	23	31	17	11
Safety	15	12	12	20	7	6
Quality Control/Assurance	9	7	4	11	4	6
Resource Requirements	21	13	12	14	14	8

The final ranking of the processes and their associated figure-of-merit scores are shown in Table 28. The final ratings suggest four general groupings of the processes. Borosilicate glass, the simplest and highest overall rated process of those evaluated, and FUETAP concrete can be categorized as relatively simple processes; glass marbles in a lead matrix and high-silica glass as moderately complex; crystalline ceramics (SYNROC and tailored ceramic) as complex; and coated sol-gel particles as very complex. These results compare favorably with two other analyses described earlier,[12,19] which also assessed the relative merits of candidate waste form production processes (Table 33).

TABLE 33.

COMPARISON OF PROCESSABILITY ANALYSIS WASTE FORM RANKINGS WITH PREVIOUS PROCESS ANALYSES

	Processability Rankings				
	This Evaluation			Other Ratings[a]	
	Ranking	FOM	Range	DP-1545[b]	PNL-3477[c]
Borosilicate Glass	1	83	78-86	77 (1)	75
FUETAP Concrete	2	77	67-78	77 (2)	65
Glass Marbles in a Lead Matrix	3	58	52-65	67 (3)	59
High-Silica Glass	4	51	45-57	57 (4)	-
Crystalline Ceramics	5	42	37-45	32 (6)	28
Coated Particles	6	32	27-32	47 (5)	-

a. Adjusted to make 100 the perfect score.

b. Reference 12.

c. Reference 19.

COMBINED PRODUCT PERFORMANCE AND PROCESSABILITY RATINGS

The processability analysis rating method was structured to be compatible with the rating procedure used in the product performance evaluation. This permitted combining the results from the two evaluations to give an overall comparative assessment of the seven candidate waste forms based on both product and process considerations. A single combined figure-of-merit rating for each waste form was obtained by calculating the geometric mean of the two individual scores. The individual and combined figure-of-merit ratings are shown in Table 34.

The combined scores were calculated as geometric means rather than simple arithmetic means in order to provide a realistic representation of the overall merit of the waste forms. Geometric means more effectively take into account poor product and/or process ratings and penalize any wide disparity between individual product and process scores. Thus, the fact that a waste form ranked highly for product performance but is extremely difficult to produce, or that a highly ranked process produces a relatively less durable form, is accounted for in the overall figure-of-merit. As can be seen in Table 34, forms such as the crystalline ceramics and coated particles which have the highest performance ratings, are lowered in the overall rating because of the inherent complexity of the required production processes. Similarly, FUETAP concrete, while requiring a relatively simple process, is ranked low because of its poor product performance rating. The high process rating for borosilicate glass and the intermediate product performance score resulted in its overall top ranked position.

TABLE 34

FINAL PRODUCT, PROCESS, AND COMBINED FIGURE-OF-MERIT SCORES FOR THE SEVEN CANDIDATE WASTE FORMS

Waste Form	Product	Process	Combined[a]
Borosilicate Glass	67	83	75
SYNROC	95	42	63
Tailored Ceramic	93	42	62
High-Silica Glass	64	51	57
FUETAP Concrete	39	77	55
Coated Particles	87	32	53
Glass Marbles in a Lead Matrix	40	58	48

a. Geometric mean

CONCLUSIONS

The results of each of the four major inputs discussed in this report served as the bases for screening and comparing the seven final candidate waste forms being developed in the National HLW Technology Program. These inputs were: 1) the preliminary waste form evaluations for defense and commercial HLW, 2) the Alternative Waste Form Peer Review Panel reviews and recommendations, 3) the product performance evaluation, and 4) the processability analysis. Based on the various results of each of these considerations, two of the seven final forms were selected for further advanced development.

First, borosilicate glass was selected for continued development as the reference form for the DWPF. The bases for this selection are as follows:

1. The process for fabricating the borosilicate glass waste form is the simplest and least expensive of all those considered.

2. Borosilicate glass performance properties rated well relative to the other forms.

3. Borosilicate glass was rated as the preferred form for HLW immobilization by the Alternative Waste Form Peer Review Panel.

4. Borosilicate glass was consistently selected as the preferred form by the DOE defense-sites, and it was rated highest in the commercial waste form evaluations.

Second, the crystalline ceramic forms, although ranking rather low in processing, were chosen as the best alternatives to borosilicate glass. The bases for this selection are as follows.

1. The crystalline ceramic forms, SYNROC and tailored ceramic, ranked highest in the product performance evaluation, and have some characteristics potentially superior to glass.

2. The ceramics have generally better high-temperature leaching characteristics than borosilicate glasses.

3. A number of mineral analogues of the crystalline ceramics have proven extremely durable in nature.

4. The SYNROC form, rated second by the Alternative Waste Form Peer Review Panel, was judged to be the best characterized and understood of the forms other than borosilicate glass.

5. Ceramic waste forms consistently ranked high in each of the DOE defense-site evaluations.

6. The ceramics are sufficiently different from glass that any unexpected problems related to glass as a waste form that might be found in the future would be unlikely to affect the ceramic forms in the same way.

A technically-based distinction between the two ceramic forms could not be made from the available characterization data. SYNROC, the more developed and characterized form, was selected as the base ceramic for an Integrated Ceramic Waste Form Development Program. This program has the goal of developing an optimized ceramic form and process using the expertise of both ceramic developers, Lawrence Livermore National Laboratory and Rockwell International. The optimized form would then incorporate the strengths of both the SYNROC and the tailored ceramic forms. This work is currently proceeding under the direction of the DOE Savannah River Operations Office, acting as lead site for the National HLW Technology Program. Initial efforts will be directed toward product and process development for immobilizing Savannah River Plant HLW. Later, efforts will be directed toward product and process development applicable to the other DOE defense-sites, as well as potential future commercial HLW, as part of the National Program goal of immobilizing all U.S. HLW.

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APPENDIX A

PRODUCT PERFORMANCE EVALUATION SENSITIVITY ANALYSES

The following are descriptions of sensitivity analyses of the effects of various assumptions made to evaluate waste form characterization data, and to determine the final product performance ratings. Sensitivities to uncertainties in the data are also addressed.

Sensitivity to Leach Rate Data

The leaching data incorporated in the data matrix were generated by MCC static leach tests using standardized leachants. Actual leaching conditions in a waste repository may be different, due to thermal, electrochemical, or solubility effects and the presence of other barriers to waste release. In addition, uncertainties are introduced by the analyses of a limited number of short-term tests, performed on laboratory-scale waste forms at multiple laboratories. Leach rates of waste forms produced by a full-scale process may be different from those measured for the products tested for this evaluation. Long-term leaching may also be only poorly simulated by short-term tests, which tend to emphasize transient leaching phenomena.

Prior to provisional approval of the MCC static tests, a "Round Robin" leach test program was performed to assess the accuracy and precision of the MCC-1 procedure. This program compared leaching results for a standard National Bureau of Standards glass, a simulated waste glass for commercial HLW, and a Columbia Basin basalt. Round Robin test results demonstrated that with a large number of laboratories reporting data, the inter-laboratory variability for most leached elements can range from about a factor of two to a factor of ten.[31] This variance is due primarily to the test procedure, rather than to analytical uncertainties.

To demonstrate the sensitivity of the evaluation procedure to assumed leach rates, the data for borosilicate glass, SYNROC, tailored ceramic, and high-silica glass were varied by a factor of ten in each direction for both the Thermal Pulse and Geologic time periods. Results are shown in Tables A-1 and A-2.

In the Thermal Pulse period, a ten-fold change in one waste form's leach rate would cause a shift of 9 to 14 points in its FOM score, relative to the other forms. During the Geologic period, the shift could be as large as 20 points. Therefore, delineation among waste forms within a given rating category was not possible.

TABLE A-1.

EFFECTS OF VARYING THERMAL PULSE PERIOD LEACH RATES

Waste Form and Change in Leach Rate		Product Performance Figure-of-Merit			
		Borosilicate Glass	SYNROC	Tailored Ceramic	High-Silica Glass
Borosilicate Glass	x10	57	95	93	64
	x1	67	95	93	64
	x0.1	71	86	84	57
SYNROC	x10	67	84	93	64
	x1	67	95	93	64
	x0.1	58	97	82	56
Tailored Ceramic	x10	69	97	82	66
	x1	67	95	93	64
	x0.1	57	84	93	55
High-Silica Glass	x10	67	95	93	55
	x1	67	95	93	64
	x0.1	61	88	86	71

TABLE A-2.

EFFECTS OF VARYING GEOLOGIC PERIOD LEACH RATES

Waste Form and Change in Leach Rate		Product Performance Figure-of-Merit			
		Borosilicate Glass	SYNROC	Tailored Ceramic	High-Silica Glass
Borosilicate Glass	x10	57	95	93	64
	x1	67	95	93	64
	x0.1	83	93	91	60
SYNROC	x10	69	79	96	66
	x1	67	95	93	64
	x0.1	57	95	77	54
Tailored Ceramic	x10	67	95	77	64
	x1	67	95	93	64
	x0.1	57	79	96	55
High-Silica Glass	x10	67	95	93	54
	x1	67	95	93	64
	x0.1	66	93	91	80

Sensitivity to Waste Loading and Mechanical Stability Data

Uncertainties in Mechanical Stability and Waste Loading have much less effect than the experimental error in leach tests. Changing the waste loading by ±50% did not yield as much as half a point change.

Unavailable Characterization Data

Comparative data were unavailable for thermal and radiation stabilities, solubilities, and the leaching of several radionuclides identified as important by the IWG. Two methods could be used to treat these performance categories:

1. Eliminate the categories, and renormalize the remaining categories; or

2. Give all waste forms full credit (worth scores of unity) for these performance factors.

FOM scores calculated by these two methods are illustrated in Table A-3. Very little differentiation is shown between waste forms using the second method. Additionally, this method would involve equating all of the waste forms for the categories for which data were unavailable. Therefore, the first method was adopted so that the waste forms were not evaluated for data which did not exist, and to allow a roughly equal effect from the relative ratings in the product performance and processability evaluations.

Anomalously High Detection Limits

Different detection limits reported by the laboratories supplying the leaching data complicated the comparison of waste form performance. One leaching category that was particularly affected was brine leaching at 40°C. A more extensive set of data was available at 90°C, and two methods were considered for replacing several anomalously high limits at 40°C.

First, it could be assumed that borosilicate glass and SYNROC would not leach more readily at the lower temperature, under otherwise identical conditions. High detection limits at 40°C could then be replaced by lower values measured at 90°C. This method was adopted.

Second, lower leach rate values could be generated by assuming that the temperature dependences for brine leaching should be similar to those measured in silicate water. This assumption was rejected because the actual leaching mechanisms for the forms are relatively unknown. These treatments of 40°C brine data, as well

TABLE A-3.

TREATMENT OF IWG CATEGORIES WITHOUT DATA

Method 1: Eliminate categories without data, renormalize to a "perfect" FOM score of 100

Method 2: Assign full credit to every waste form for categories without data

Waste Form	Product Performance Figure-of-Merit	
	Method 1	Method 2
Borosilicate Glass	67	88
SYNROC	95	98
Tailored Ceramic	93	97
High-Silica Glass	64	87
FUETAP Concrete	39	77
Coated Particles[a]		
Glass Marbles in a Lead Matrix[a]		

a. Few leaching data available

as the normal assumptions for handling detection limits, are shown in Table A-4. The FOM scores of the glass forms are lowered somewhat by these variations, because this category is no longer effectively eliminated by the high limits.

Detection Limits Considered as Actual Values

Raising a waste form's leaching data to the level of another form's detection limit altered the product performance ratings from what they would be if analyses were not affected by limits. However, the variation was not sufficiently severe to change the relative rankings of waste forms, especially after combination with the processability ratings.

Product FOM ratings were calculated by assuming that leach rates were exactly equal to reported limits. Reported values for other waste forms were not changed. These ratings are compared with the results from the accepted FOM method in Table A-5. This formalism would allow the tailored ceramic form full credit for its low measured leach rates for strontium at 90°C, and that form would then lead the product rankings.

Coated Particle Leaching

The coated particle waste form was accommodated in the leach rate comparisons by assigning fractional release rates equal to the best of the other forms in each category and time period. A more exact physical model was also used to determine whether the overall rankings were affected by this assumption. Some portion of the particle coatings in this waste form product would be imperfect. After processing, handling, and previous thermal and leaching history, an even larger portion of the coatings must be presumed to have failed, before or during the Geologic time period. The Geologic period is assumed to commence approximately 1000 years after waste emplacement; the radiological hazard of the waste will not further decline significantly for a long period. The leaching environment cannot be predicted exactly over geologic time scales. However, degradation of coatings would occur in groundwaters that are within the range of those considered possible in a nuclear waste repository.

Leaching of the coated particle waste form in the Geologic time period was modeled by assuming that some fraction of the coatings have failed, exposing the waste-containing ceramic kernel to leaching. The kernel was assumed to leach at the same rate as SYNROC, the waste form it most closely resembles. The fraction of coatings assumed to have failed was varied between one part in 100,000 to unity. The lowest failed fraction, 10^{-5}, was

TABLE A-4.

TREATMENT OF 40°C BRINE LEACHING DATA

Method 1: Apply normal rules for detection limits

Method 2: Replace 40°C limits with 90°C data if 90°C data are lower

Method 3: Replace 40°C limits with values calculated from 90°C data and temperature dependence observed in silicate water leaching

Waste Form	Product Performance Figure-of-Merit		
	Method 1	Method 2	Method 3
Borosilicate Glass	72	67	69
SYNROC	95	95	95
Tailored Ceramic	93	93	93
High-Silica Glass	71	64	64
FUETAP Concrete	48	39	40
Coated Particles[a]			
Glass Marbles in a Lead Matrix[a]			

a. Few leaching data available

TABLE A-5.

TREATMENT OF DETECTION LIMITS

Method 1: Apply normal rules for detection limits

Method 2: Compare data directly, making no adjustments for limits

Waste Form	Product Performance Figure-of-Merit	
	Method 1	Method 2
Borosilicate Glass	67	55
SYNROC	95	90
Tailored Ceramic	93	96
High-Silica Glass	64	54
FUETAP Concrete	39	33
Coated Particles[a]		
Glass Marbles in a Lead Matrix[a]		

a. Few leaching data available

considered to be beyond the best coating success rate that could be assumed as a basis for process design.

The product performance FOM scores are shown in Table A-6, as a function of failed coatings in the Geologic period. The ratings of the two ceramic forms equal that of the coated particles at a failed fraction between 0.5 and 1 percent. When these ratings are combined with the processability ratings, the combined rating for coated particles only equals those of the crystalline ceramics at the smallest failed fraction, 10^{-5}. The ceramics would demonstrate an advantage in the combined rankings for failed fractions exceeding 10^{-4}.

Glass Marbles in a Lead Matrix

Few data were available for the leaching of simulated waste from metal matrix waste forms. Also, the ability of the lead matrix to prevent the exposure of leachable glass marble surfaces would depend on the previous history of the waste form.

One advantage of the matrix form over borosilicate glass was expected to be the increased thermal conductivity, which could better remove decay heat and lower waste form centerline temperatures. Thermal stability performance data were unavailable, however. The thermal loading of waste forms for SRP HLW will be much lower than for reprocessed HLW from commercial nuclear reactors, and centerline temperatures of glass would not be expected to be high enough to cause significant degradation.

Due to the complexity of long-term chemical interactions between a metal matrix, the waste form, engineered barriers, and repository groundwaters, no detailed modeling of this form was attempted. When leaching data were available, the matrix form was given full credit for low leach rates. When data were unavailable or were higher than for borosilicate glass, the leach rates for borosilicate glass were used. The matrix form's lower ranking than borosilicate glass is due to the potentially high leachable surface area of the marbles, and a lower waste loading.

TABLE A-6.

EFFECT OF FRACTION OF FAILED PARTICLE COATINGS ON RELATIVE PRODUCT PERFORMANCE RATINGS

Waste Form	Product Performance Figure-of-Merit[a]						
	Fraction of Failed Particle Coatings During Geologic Period						
	0.00001	0.0001	0.001	0.005	0.01	0.05	0.1
Borosilicate Glass	47 (68)	50 (64)	55 (68)	61 (71)	64 (73)	67 (75)	67 (75)
SYNROC	61 (51)	66 (53)	75 (56)	85 (60)	90 (62)	95 (64)	95 (64)
Tailored Ceramic	62 (51)	66 (53)	74 (56)	83 (60)	89 (61)	93 (63)	93 (63)
High-Silica Glass	44 (47)	47 (49)	52 (52)	58 (54)	61 (56)	64 (57)	64 (57)
FUETAP Concrete	22 (42)	25 (44)	29 (48)	34 (52)	37 (54)	39 (56)	39 (56)
Coated Particles	87 (53)	87 (53)	87 (53)	87 (53)	87 (53)	78 (50)	73 (48)
Glass Marbles in a Lead Matrix	30 (42)	32 (43)	34 (45)	37 (47)	39 (48)	40 (49)	40 (49)

a. Numbers in parentheses are the combined Product and Process Figures-of-Merit.