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PROCESS DESCRIPTION
AND
PLANT DESIGN
FOR
PREPARING CERAMIC HIGH-LEVEL WASTE FORMS

DOE Research and Development Report

*Prepared for the United States
Department of Energy,
Savannah River Operations Office
under Contract Number DE-AC09-79ET41900*



Rockwell International

Energy Systems Group

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NUCLEAR WASTE
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PROCESS DESCRIPTION
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FOR
PREPARING CERAMIC HIGH-LEVEL WASTE FORMS

By

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CONTENTS

	Page
I. Executive Summary.....	1
II. Introduction.....	5
III. The Ceramic Waste Form.....	7
A. Description of Ceramic Waste Form.....	7
B. Defense and Commercial Waste Compositions.....	7
C. History of Ceramic Form Development.....	10
D. Ceramic-Phase Assemblages.....	11
E. Ceramic and Glass Waste Form Characterization.....	12
IV. Neutralized Defense Waste Immobilization Processes.....	19
A. Process Modifications.....	19
1. Fluid-Bed Calcination State of the Art.....	23
2. Hot Isostatic Pressing State of the Art.....	24
B. Modified Ceramic Flow Diagram and Process Layout for Neutralized Defense Waste.....	27
1. Process Flow Diagram.....	28
2. Off-Gas Process and Cell Layout.....	30
3. Process Layout.....	33
4. Glass Process Flowsheet and Layout.....	33
C. Neutralized Defense Waste Management Costs.....	33
V. Defense and Commercial Acid Waste Immobilization and Costs.....	43
A. Acid Waste Ceramic Flow Diagram and Process Layout.....	43
1. Design Parameters.....	43
2. Fluidized-Bed Calciner.....	43
3. HIP Cans.....	45
4. Process Flow Diagram.....	47
5. Process Layout.....	47
B. Acid Waste Glass Flow Diagram and Process Layout.....	47
C. Acid Waste Ceramic and Glass Plant Processing Costs.....	51
VI. Ceramic Plant for Hanford Waste and Other High-Level Wastes.....	55
VII. Conclusions and Recommendations.....	57
VIII. References.....	61
Appendix A.....	67

TABLES

	Page
1. Typical Compositions of Savannah River Plant Defense Waste Calcines.....	8
2. Commercial High-Level Liquid and Intermediate-Level Liquid Waste Compositions and Volumes.....	9
3. Mechanical Properties of Borosilicate Glass and Ceramic.....	13
4. Thermal Properties of Borosilicate Glass and Ceramic.....	13
5. Comparative Leach Rates – Ratio of Averages of Borosilicate Glass to Ceramic Leach Rates.....	15
6. Tailored Ceramic Formulation and Calculated Phase Content for SRP High-Aluminum and Composite Defense Waste.....	17
7. Defense Waste Design Parameters.....	28
8. SRP Neutralized Government-Generated Waste Management Costs.....	38
9. Comparative Waste Management Costs – SRP Government-Generated Wastes.....	40
10. Design Values Used for Glass and Ceramic Plants Immobilizing Waste from 3000-Tonne/Year Commercial Reprocessing Plant.....	44
11. Summary of Acid Waste Immobilization Plant Capital and Operating Costs.....	53
A-1. Comparative Costs Using Glass and Ceramic Waste Forms to Manage SRP Waste.....	71

FIGURES

1. Full-Scale, New High-Level Liquid Waste Calcine Facility at INEL.....	20
2. Simulated Nuclear Waste Fluidized-Bed Calcine Produced from Waste Slurries.....	21
3. Large HIP Unit Used by ASEA to Encapsulate Spent Fuel Rods in Alumina.....	25
4. Encapsulating Simulated Spent Fuel in Ceramic.....	26
5. Ceramic Preparation Flow Diagram for Neutralized Defense Waste....	29
6. Flowsheet for Modified Ceramic Process Off-Gas System.....	31
7. Off-Gas Decontamination Cell.....	32
8. Ceramic Process Layout for Neutralized Defense Waste.....	34
9. Borosilicate Glass Process Flowsheet.....	35

DOE/ET/41900-16
(ESG-DOE-13397)

FIGURES

	Page
10. Layout of Glass Production Canyon for Neutralized Defense Waste...	36
11. HIPping Can for Commercial Waste.....	46
12. Ceramic Preparation Flow Diagram for Acid Wastes.....	48
13. Ceramic Process Layout for Acid Waste.....	49
14. Glass Production Flowsheet for Acid Waste.....	50
15. Layout of Glass Production Canyon for Commercial (Acid) Waste.....	52
A-1. Modifications Made in the Preliminary Ceramic Process Flowsheet for Defense Waste.....	68
A-2. Modifications Made in the Preliminary Crystalline Ceramic Process Cell Arrangement.....	69

ABSTRACT

The ceramics process flow diagram has been simplified and upgraded to utilize only two major processing steps – fluid-bed calcination and hot isostatic press consolidation; both are well developed. Full-scale fluid-bed calcination has been used at INEL to calcine high-level waste for 18 years; and a second-generation calciner, a fully remotely operated and maintained calciner that meets ALARA guidelines, started calcining high-level waste in 1982. Full-scale hot isostatic consolidation has been used by DOE and commercial enterprises to consolidate radioactive components and to encapsulate spent fuel elements for several years. With further development aimed at process integration and parametric optimization, the operating knowledge of full-scale demonstration of the key process steps should be rapidly adaptable to scale-up of the ceramic process to full plant size.

Process flowsheets used to prepare ceramic and glass waste forms from defense and commercial high-level liquid waste are described. Preliminary layouts of process flow diagrams in a high-level processing canyon were prepared and used to estimate the preliminary cost of the plant to fabricate ceramic and glass waste forms. The estimated costs for using the ceramic and glass options were compared for total waste management costs of SRP high-level liquid waste. Using our design, for both the ceramic and glass plant, capital and operating costs are essentially the same for both defense and commercial wastes, but total waste management costs are calculated to be significantly less for defense wastes using the ceramic option. It is concluded from this and other studies that the ceramic form may offer important advantages over glass in leach resistance, waste loading, density, and process flexibility. In addition, preliminary economic calculations indicate that ceramics must be considered a leading candidate for the form to immobilize high-level wastes. Continued development of ceramics for this purpose is warranted and recommended.

I. EXECUTIVE SUMMARY

Ceramic waste forms have the same or similar crystalline phases as naturally occurring crystalline minerals, which have endured geologic weathering for millions of years. Ceramic waste forms incorporate nuclear waste materials in the crystalline structure; this provides superior mechanical, thermal, and hydrothermal stability to amorphous noncrystalline waste forms. Radionuclides, to eliminate their radiological hazard to man, must be isolated from the biosphere until they decay to stable isotopes. Current concepts for a high-level nuclear waste management system are based on a multibarrier approach with near-field and far-field performance criteria. A superior waste form performance not only provides tradeoff on other engineered barriers and better near-field performance in upset scenarios but also offers equal or better isolation from the biosphere even if the predicted repository characteristics are such that environmental hazards are judged to be negligible because of migration times. The smaller the rate of release from the source, the less reliance one needs to make on retardation effects, migrating time, and overall repository properties.

Significant process improvements have been made in the ceramic process during the past 3 years. The process consists of two steps: fluid-bed calcination and hot isostatic press (HIP) consolidation. Both steps are well-developed, well-understood commercial processing methods. A fluid-bed calciner has been used at the Idaho National Engineering Laboratory (INEL) to solidify high-level liquid waste for 18 years and has produced over 1700 m³ (60,000 ft³) of high-level waste calcine. Hot isostatic press technology has been used in the ceramics, metallurgical, and cement industries for over 30 years. Radioactive materials and spent fuel rods are being consolidated in DOE and commercial units much larger than required for waste management. Remotization of both of these systems has been completed so that these systems could be adapted to processing canyon operation.

Flowsheets and process plant layouts incorporating these process improvements have been developed. The process improvements not only provide for improved processability and maintainability but also significantly reduce the

in-canyon space requirements. One of the major process improvements was the substitution of the fluidized-bed calciner for the spray calciner in the preliminary process flowsheet. The fluidized-bed calciner provides granules of waste oxide which are readily vibrapacked into cans for consolidation into fully dense minerals by hot isostatic pressing (HIPping). These cans can be crimp-sealed after outgassing instead of sealed by welding after tamping the spray calcine powders into the cans, as shown in the preliminary flowsheet. Furthermore, it appears that all valence adjustment requirements can be accomplished in the fluidized-bed calciner and HIP cans without adding metallic reducing agents. The uniformly sized granular product from the fluidized-bed calciner also permits better dimensional control during HIP operations.

Flowsheets and process canyon layouts were developed for the ceramic and glass options to manage commercial and government-generated high-level liquid waste. Cost comparison estimates using the improved ceramic process flowsheet indicate that capital and operating cost reductions can be made over the originally proposed ceramic process. Cost comparisons with a glass immobilization plant indicate that the improved ceramic immobilization plant requires about the same capital investment and has about the same operating costs as the glass immobilization plant. Using the cost methodology described herein, overall waste management costs for the presently existing Savannah River defense waste inventory appear to be about \$0.9 billion less expensive using the updated ceramic flowsheet compared to glass.

The first cost estimate for managing SRP high-level waste utilizing the ceramic option was made by the DuPont Engineering Department and estimated to be \$2.9 billion. LLNL reduced this estimate by different allocation of contingencies and repository costs to \$2.1 billion. The further reduction in this report to \$1.6 billion resulted from a redesign of the ceramic plant and a reduction in contingencies because full-scale demonstration of the major process steps has been accomplished. It should be noted that all waste management costs are dependent on repository costs, which are still undetermined. However, whatever decisions are made on repository cost allocations, the ceramic option is less dependent on these decisions because of its capacity for high waste loading.

For an immobilization plant tied to a reprocessing plant where throughput is constrained by the reprocessing plant waste production rate, the capital and operating costs are similar but somewhat less for a ceramic plant than for a glass plant; however, the differences are within the error of the estimates. When the overall waste management costs are considered, however, the cost savings realized in transportation and at the repository should also make commercial waste management based on a ceramic form more cost effective than commercial waste management based on a glass form.

The flexibility of the ceramic process for immobilization of widely varying waste streams with high thermal loadings and the modularizability, compactness, and simplicity of process components are major advantages of the ceramics process. The high waste loading and density of ceramic waste forms substantially increases the process throughput which can be designed into a plant with overall size constraints of fitting into existing process cells. Furthermore, the high waste loading and density significantly reduce the number of waste packages which must be stored until a repository is operational. This, plus possible favorable overall economics and the current state of development of the ceramic process, makes the ceramic process a potential candidate for nuclear reprocessing waste management.

II. INTRODUCTION

Management of nuclear reprocessing wastes includes immobilizing the radionuclides in waste form monoliths and emplacing the waste forms in a geologic repository.⁽¹⁻⁵⁾ Glass⁽⁶⁻²⁰⁾ has been investigated as the waste form for the past 30 years. Recently, ceramic assemblages⁽²¹⁻³⁵⁾ of natural minerals^(36,37) have been investigated as an alternate waste form. The alternate ceramic waste process, although not as well developed as the glass process, has numerous advantages that warrant its continued development. Some of the advantages are:

- 1) Superior evidence of long-term immobilization of nuclides since the radwaste ceramics are analogues of natural minerals that have existed for geologic times under geologic conditions of pressure, temperature, and hydrology.^(36,37)
- 2) Ceramics have a higher density⁽³⁸⁻⁴⁰⁾ and can have a much higher waste loading⁽³⁸⁻⁴⁰⁾ than glass and, therefore, reduce the resultant number of waste packages that must be produced, transported to a repository, and emplaced in a repository by at least a factor of three. Thus, radiation exposure of the public during transportation and to workers during production, transportation, and emplacement can be reduced.
- 3) Leach rates by Materials Characterization Center (MCC) tests show that long-lived nuclides are up to three orders of magnitude more effectively insolubilized by ceramics than by glass.^(41,42) This could be important in preventing long-lived radionuclides from entering the biosphere from a repository,⁽⁴³⁻⁵¹⁾ particularly in upset situations.
- 4) Although not demonstrated for long-term integrated operation, it is expected that the ceramic process to immobilize high-level radioactive waste will be simpler than the glass process and, therefore, will have processing advantages. For example, no molten materials are handled as required in the glass melter; and therefore the periodic, approximately biannual-to-triannual rebuilding of the glass melter is avoided. Furthermore, in the ceramics

process line, the highly radioactive product is contained in sealed containers during all processing steps except calcining; therefore, contamination of the processing canyon and volatilization of volatile nuclides is expected to be minimized.

- 5) The overall waste management costs using the ceramic waste form by our analysis is less than the waste management costs using the glass waste form. This cost advantage is sensitive to repository cost allocations which are still undetermined. However, whatever repository decisions are made, the ceramic option is less dependent on these future decisions because of its high waste loading capability.

This report is one of three substantiating these advantages. The other two deal with the preparation and characterization of the waste form⁽⁴¹⁾ and waste management systems analysis and economics.⁽⁵²⁾ After a description of the ceramic waste form and preliminary defense waste form flowsheet and comparative glass-ceramic defense waste management economics, the proposed commercial ceramic process flowsheet and comparative costs of the glass-ceramic immobilization plants are discussed.

III. THE CERAMIC WASTE FORM

A. DESCRIPTION OF CERAMIC WASTE FORM

Ceramic waste forms^(21-35,41) are crystalline-phase assemblages with the same or similar phases as natural minerals that have endured geologic conditions for millions of years, often under high temperatures and high pressures. Thus, ceramic waste forms should be capable of isolating the waste radionuclides from the environment for similarly long periods under the geologic conditions of a repository.

The Department of Energy, in the draft Environmental Impact Statement for Management of Commercially Generated Radioactive Waste,⁽⁵⁰⁾ conducted a survey of naturally occurring minerals which have maintained their integrity for geologic times. This report lists those minerals which resist weathering or dissolution and occur naturally in igneous, sedimentary, metamorphic, or placer deposits. These minerals are potential hosts for radionuclides.

In general, several different minerals can be used to immobilize radionuclides for biosphere isolation. This has led to the use of different mineral assemblages for different nuclear wastes. In general, the Synroc ceramics developed by the Australian Atomic Energy Agency⁽²⁵⁻²⁷⁾ and Lawrence Livermore National Laboratory^(29,30) consist of titania-based minerals, while the mineral assemblages proposed by Rockwell^(31-34,37,40,41) are iron-alumina- or iron-titania-based ceramics.

B. DEFENSE AND COMMERCIAL WASTE COMPOSITIONS

The variation in chemical composition of Savannah River Plant (SRP) defense high-level radioactive waste is illustrated in Table 1, where the composition of major elements in SRP waste is given with and without alumina removal. Partial sodium and aluminum removal is planned in the glassification program. Except for uranium, the radioactive portion of the waste is less than 1%; the major components are reprocessing and neutralization chemicals as seen in Table 1.

TABLE 1
TYPICAL COMPOSITIONS OF SAVANNAH RIVER PLANT DEFENSE WASTE CALCINES

Component	Major Elements Only					
	Without Al Removal (wt. %)			With Al Removal (wt. %)		
	High Fe	Composite	High Al	High Fe	Composite	High Al
Fe ₂ O ₃	57.17	36.13	5.32	55.90	47.16	14.80
Al ₂ O ₃	4.89	28.26	76.05	1.29	9.24	50.77
MnO ₂	3.56	9.94	4.37	3.74	12.98	12.16
U ₃ O ₈	12.34	3.26	1.28	12.98	4.25	3.57
CaO	3.62	2.69	0.35	3.80	3.51	0.97
NiO	9.08	4.47	0.78	9.54	5.84	2.17
SiO ₂	0.40	0.85	0.56	<0.40	1.12	1.57
Na ₂ O	4.52	5.08	1.96	4.75	6.63	5.41
Na ₂ SO ₄	<0.50	0.93	<0.50	<0.50	1.21	<0.50
Ion-Siv IE-95*	8.82	8.93	9.33	8.00	8.05	8.58

*Mixture of CaAl₂Si₄O₁₂·6H₂O and (NaKCa)₃Al₃Si₈O₂₄·8H₂O

Eventually, the reprocessing waste will be immobilized directly from the acid state without neutralization; this will eliminate most of the sodium from the reprocessing waste (Table 1) and eliminate the need and cost associated with washing the neutralized waste. Commercial reprocessing plants are designed to utilize methods which minimize the use of reprocessing chemicals which produce stable (nonradioactive) chemical oxide residues in the waste and, therefore, increase the fission product and resultant heat contained in concentrated liquid waste. For example, the concentrated waste stream shown in Table 2 from a hypothetical modern reprocessing plant contains over 40 wt. % fission product oxides when calcined.

As shown in Tables 1 and 2, the waste composition from different reprocessing plants and reprocessing campaigns from the same plant can be quite different.

TABLE 2
 COMMERCIAL HIGH-LEVEL LIQUID AND INTERMEDIATE-LEVEL
 LIQUID WASTE COMPOSITIONS AND VOLUMES

	HLLW		ILLW*
	Nominal	Minimum	
Fission products less I (g/l)	67.67	45.07	
Iodine at 0.5% (g/l)	0.0032	0.0022	0.0043
Uranium at 0.5% loss (g/l)	12.69	8.45	16.91
Plutonium at 0.5% loss (g/l)	0.117	0.076	0.152
Other actinides (g/l)	1.75	1.17	0.0035
Soluble poison (g/l)	64.22	42.77	
Nitric acid (M)	4-7	4-7	2.5
Total nitrate at max. HNO ₃	10.54	9.25	3.5
Phosphate (g/l)	0.45	0.30	23.0
Shear fines (g/l)	0.66	0.44	
Corrosion products (g/l)	0.65	0.43	0.17
Chloride (g/l)	0.053	0.035	0.32
Sodium [potassium] (g/l)			17.64 [0.36]
Manganese (g/l)			0.5
Sulfate (g/l)			0.11
Decay heat (watts/l, after 7.5 years cooling)	3.13	2.51	0.012
Est. insoluble solids (g/l)	14.6	9.7	2.0

*Intermediate-level liquid waste (ILLW) is generated during cleanup of the organic extractant and solvent for recycle to the reprocessing system.

Thus, it is important that the waste immobilization method be able to accommodate vastly different waste compositions with different properties such as decay heat. As will be shown below, the ceramic waste form has excellent capability to accommodate wastes of widely varying compositions and properties.

C. HISTORY OF CERAMIC FORM DEVELOPMENT

With the recognition that borosilicate glass is inherently unstable in ground water at temperatures above 100°C, work began in the early 1950s on developing a waste form stable over geologic time scales in a repository environment. Out of this research came the original concept of immobilizing high-level nuclear waste in a crystalline ceramic form, proposed in 1953 by L. P. Hatch⁽⁵¹⁾ and developed by McCarthy^(23,53) and Roy.⁽⁵⁴⁾ The original efforts were based on producing a ceramic form consisting of thermodynamically stable crystalline phases with lattice host sites for each of the waste elements. Implicit in this concept was the use of additives to chemically alter the composition of a nuclear waste to produce the desired phase assemblage upon consolidation. Ringwood and coworkers⁽²⁵⁻²⁷⁾ in 1977-1978 developed a slightly different approach to the design of the ceramic form. They selected an assemblage of structures isomorphic with the natural minerals hollandite, zirconolite, and perovskite, known to be stable over geologic ages, and prepared them synthetically. They included dilute concentrations of fission products and actinides in forms prepared for testing and characterization. This material, called "Synroc" or synthetic rock, was designed to retain the properties of the natural minerals while hosting fission products and actinides at levels up to approximately 20 wt. % as oxides. The efforts of Ringwood and coworkers established the potential of the ceramic form for high leach resistance and geochemical stability but was somewhat academic in that only fission products and actinide simulants were diluted into the mineral phases, while reprocessing chemicals, which are major waste components, were omitted.

D. CERAMIC-PHASE ASSEMBLAGES

The major portion of all existing U.S. high-level wastes such as those at Savannah River, Hanford, and NFS* are primarily composed of the nonradioactive materials (Na, Al, Fe, Si, etc.) added during reprocessing. This fact was recognized by both Rockwell International and the Lawrence Livermore National Laboratory in the initial development of a polyphase ceramic form for Savannah River Plant defense wastes under DOE sponsorship in the Alternate Waste Form Development Program. LLNL proceeded to develop a ceramic form based on the original Synroc, deleting and adding phases as required to accommodate the SRP waste components. Rockwell, however, took and is still utilizing a unique approach to the design of the ceramic form that is to base the final ceramic-phase assemblage on those naturally occurring stable phases which the waste elements, including the nonradioactive components, most readily form, rather than diluting the waste into a small set of predetermined phases. This approach immediately increased the waste loading available in the ceramic significantly, while simplifying the required processing control.⁽⁵⁵⁾

An example of this approach was the "high alumina" ceramic form prepared by Rockwell in 1979 from simulated Savannah River Plant "high Al composition" waste. The ceramic was composed of 90 wt. % waste oxide components and consisted of only three natural mineral phases: uraninite, hercynite spinel, and magnetoplumbite.⁽⁵⁵⁾ This material showed the best overall leach and mechanical impact resistance of all waste forms tested in the 1981 Alternate Waste Form Peer Review Panel evaluation.⁽⁵⁶⁾ The high waste loading offered the possibility of a significant cost advantage since the thermal content of the SRP waste is low. This same approach, when applied to the SRP "high Fe" and "composite" waste compositions, produced a form able to accommodate 50 to 70 wt. % waste at a density of 4 g/cm³ with only four phases: nepheline, spinel (hercynite-magnetite), uraninite, and magnetoplumbite.⁽³²⁾

*Nuclear Fuels Services plant at West Valley, New York

LLNL, approaching the same waste compositions from Ringwood's perspective and striving for higher waste loadings, reached a very similar result by modifying their original assemblage as the waste dictated. The final Synroc-D form contained two of the Rockwell phases, nepheline and spinel, and two of the original Synroc phases, perovskite and a modified zirconolite, also at a waste loading of about 60 wt. % waste.⁽³⁵⁾

The Rockwell and LLNL efforts to develop ceramic waste forms were combined in October 1981. The final form represents the best combination of the Rockwell and LLNL forms and has demonstrated leach resistance 100 to 1000 times superior to borosilicate glass for uranium at 3 times the waste loading in the waste form.^(41,42) Moreover, it was demonstrated that great flexibility in redox control and consolidation conditions greatly reduce the process complexity.^(33,41) The leach resistance of the ceramic forms and their dissolution mechanisms have also been studied in depth.⁽³⁴⁾ These data indicate that the ceramic forms would retain actinides over geologic time scales even under hydrothermal exposure.

Rockwell has been applying the same approach used in ceramic design for defense waste to commercial waste compositions. In contrast to the Australian efforts in which only fission products are incorporated into the Synroc forms, Rockwell has designed and is testing a ceramic form for the reference Barnwell AGNS reprocessing waste stream (Table 2). This waste stream contains a large fraction of nonradioactive material (Gd_2O_3 , Na_2O , P_2O_5 , etc.) in addition to the fission products and actinide elements. The current Rockwell form contains only three major phases: rutile, pyrochlore, and perovskite, and uses titania as the main additive. This waste form is capable of extremely high waste loadings (about 70 wt. %) and densities (up to 5.4 g/cm^3) and is exhibiting superior radionuclide leach resistance.

E. CERAMIC AND GLASS WASTE FORM CHARACTERIZATION

The physical and thermal properties for both ceramic and glass waste forms⁽⁴²⁾ are given in Tables 3 and 4. In general, the ceramic waste form has both superior mechanical and thermal properties (tensile strength, thermal conductivity,

TABLE 3
MECHANICAL PROPERTIES OF BOROSILICATE GLASS AND CERAMIC⁽⁴²⁾

Property	Borosilicate Glass	Ceramic ^a
Tensile strength (MPa) ^b	62.1	75.9 ^c
Compressive strength (MPa)	550	280
Young's Modulus ^d (GPa)	66.9	139
Poisson's ratio ^e	0.18	0.28
Density (g/cm ³)	2.75	4.00

^aPrepared at LLNL with 69 wt. % loading of SRP composite sludge without aluminum removal (see Table 1).

^b1 MPa = 145.0 psi.

^cFor Synroc-C, Synroc formulation for simulated commercial power reactor waste.

^dYoung's Modulus, the modulus of elasticity, measures the stiffness of the material.

^ePoisson's ratio is the ratio of equatorial to axial strain under an applied axial stress.

TABLE 4
THERMAL PROPERTIES OF BOROSILICATE GLASS AND CERAMIC⁽⁴²⁾

Property	Borosilicate Glass	Ceramic
Thermal conductivity (W/m·K)	0.95 (100 ^o C)	1.85 (20 ^o C) 1.91 (200 ^o C)
Heat capacity (J/g·K)	0.83 (25 ^o C)	0.74 (20 ^o C)
Thermal diffusivity (m ² /s)	3.8 x 10 ⁻⁷	6.5 x 10 ⁻⁷
Linear thermal expansion coefficient (°C ⁻¹)	10.9 x 10 ⁻⁶	11 x 10 ^{-6*}
Softening point (°C)	502	--
Solidus temperature (°C)	--	1270

*For 22-950^oC

and heat capacity) and withstands impingement tests much better than glass. It does not soften and can withstand temperatures in excess of 1000°C without any degradation of properties or instability of ceramic phases.

The relative leach rates for 28-day tests of borosilicate glass and ceramics are given in Table 5. In general, except for cesium, calcium, and strontium, the ceramic leach rates are significantly lower (i.e., the glass-to-ceramic leach rate ratio is greater than one) and are up to three orders of magnitude lower for the actinide uranium. Further improvements have been made in ceramics since these samples were made, which indicate that even lower leach rates for ceramics can be obtained,⁽⁴¹⁾ particularly for cesium, calcium, and strontium. In fact, it has been shown that leach rates from ceramics are diffusion-controlled, whereas leach rates from glass are solubility-controlled.⁽⁴¹⁾

Thus, the leach rate of the long-term hazards to man (actinides and their decay products)⁽⁴⁷⁻⁴⁹⁾ found in nuclear waste will be effectively immobilized in the waste form with extrapolated leach rates of less than 10^{-5} of the contained radionuclides per year. Thus, the repository emplacement of ceramic waste forms may not require overpacks, which should reduce waste management costs even further.

In general, the repository depends upon a number of barriers to effectively isolate radioactive waste from the biosphere. However, in an upset condition, the most important barrier and in some cases the only barrier that can be relied upon to isolate these hazards from the biosphere is the waste form itself. The superior leach resistance of ceramic waste would effectively isolate these hazards in upset conditions and provide an additional margin of safety under nonupset scenarios.

The high waste loading of ceramics is illustrated in Table 6, where the composition of ceramic defense waste forms for high-aluminum and composite wastes are given. Note that waste loading of approximately 90 wt. % can be obtained for high-alumina wastes and about 65 wt. % for composite wastes. Recent experiments indicate that waste loadings of over 75 wt. % and densities of over 5.6 g/cm³ can be obtained for commercial waste ceramics without decreasing the radionuclide leach resistance.⁽⁴¹⁾

TABLE 5
COMPARATIVE LEACH RATES — RATIO OF AVERAGES OF BOROSILICATE GLASS TO
CERAMIC LEACH RATES⁽⁴²⁾

Nuclide	Temperature (°C)	Leachant	Ratio of Glass to Ceramic Leach Rates (MCC-1,2)*		
			Composite	High Al	High Fe
Cs	40	Deionized water	0.26	0.002	6.3
		Silicate Water	0.4	-	-
		Brine	>0.4	-	-
	90	Deionized water	1.4	0.14	3.8
		Silicate water	1.9	0.068	3.3
		Brine	>1.1	0.041	3.9
	150	Deionized water	0.94	-	-
		Silicate water	3.1	-	-
		Brine	1.8	-	-
Sr	40	Deionized water	<0.001	-	-
		Silicate water	<0.03	-	-
	90	Deionized water	<0.003	-	-
		Silicate water	<0.01	-	-
	150	Deionized water	<0.002	-	-
		Silicate water	<0.01	-	-
U	40	Deionized water	-	>0.2	>57
		Silicate water	400	-	-
	90	Deionized water	1200	>8	>420
		Silicate water	1000	>70	600
		Brine	22	-	-
	150	Deionized water	2800	-	-
		Silicate water	>44	-	-
		Brine	190	-	-
	Mn	90	Deionized water	0.34	-
Silicate water			>13	-	-
Brine			>27	-	-
150		Deionized water	0.3	-	-
		Brine	5.1	-	-
Ca		90	Deionized water	<0.035	-
	Silicate water		<0.11	-	-
	150	Deionized water	0.067	-	-
		Silicate water	<1.3	-	-

TABLE 5
 COMPARATIVE LEACH RATES — RATIO OF AVERAGES OF BOROSILICATE GLASS TO
 CERAMIC LEACH RATES (42)
 (CONTINUED)

Nuclide	Temperature (°C)	Leachant	Ratio of Glass to Ceramic Leach Rates (MCC-1,2)*		
			Composite	High Al	High Fe
Na	40	Deionized water	-	>0.01	6
		Deionized water	4	>0.2	>7
	90	Silicate water	2	0.3	62
	150	Deionized water	4	-	-
		Silicate water	60	-	-
	Si	90	Deionized water	2.5	-
Silicate water			4.2	-	-
Brine			>1.3	-	-
150		Deionized water	2.0	-	-
		Silicate water	3.2	-	-
		Brine	0.52	-	-
Al	40	Deionized water	14	1	8
		Deionized water	1.8	12	3
	90	Silicate water	2.6	7.1	2
	150	Deionized water	2.5	-	-
		Silicate water	5.6	-	-
		Brine	>1700	-	-
Fe	40	Deionized water	-	10	4
		Deionized water	-	<31	-
	90	Silicate water	>2	-	-
	150	Deionized water	3	-	-
		Silicate water	2	-	-
	Zr	40	Deionized water	-	1
Deionized water			18	3	25
90		Silicate water	8	10	7
		Silicate water	8	10	7
		Brine	4	4	7

*Materials Characterization Center (MCC), Pacific Northwest Laboratory, Richland, Washington, has developed several standard tests to determine and compare waste form properties.

TABLE 6
 TAILORED CERAMIC FORMULATION AND CALCULATED PHASE CONTENT FOR
 SRP HIGH-ALUMINUM AND COMPOSITE DEFENSE WASTE

Component Oxide	High Alumina		Composite	
	Waste Oxide (wt. %)	Additives (wt. %)	Waste Oxide (wt. %)	Additives (wt. %)
Fe ₂ O ₃	5.05		25.11	
Al ₂ O ₃	72.88		19.64	28.31
MnO ₂	4.18		6.91	
U ₃ O ₈	1.22		2.26	
CaO	0.67		1.87	
NiO	0.75		3.11	
SiO ₂	0.90		0.89	6.20
Na ₂ O	0.91		3.03	
Na ₂ SO ₄			0.60	
SrO	0.18		0.26	
Cs ₂ O	0.18		0.26	
Cs ₂ O ₃	0.34		0.53	
Nd ₂ O ₃	0.34		0.53	
La ₂ O ₃		9.90		0.29
ZrO ₂		0.50		0.20
TiO ₂		2.00		
Total	87.60	12.40	65.00	35.00
Calculated Phase Content				
Phase	High Alumina		Composite	
	(wt. %)	(vol %)	(wt. %)	(vol %)
Magnetoplumbite	60.0	63.0	29.6	30.7
Spinel Solid Solution	21.4	20.1	52.5	45.9
Uraninite	1.7	0.7	2.4	0.9
Corundum	16.9	16.2	--	--
Nepheline	--	--	15.5	22.5

IV. NEUTRALIZED DEFENSE WASTE IMMOBILIZATION PROCESSES

A preliminary ceramic process flow diagram was used in the Alternative Waste Form Assessment program. Since very little process development work had been completed, a conservative approach was used in the preliminary flow diagram developed and the processing equipment used was not optimized for the ceramic waste form. Since this preliminary flowsheet and environmental assessment document were prepared,⁽⁵⁹⁾ a number of process improvements have been made, and a modified flowsheet has been developed. However, these changes were not incorporated due to the short time schedule allowed for the initial process and cost comparison with the reference glass process for immobilization of neutralized defense waste.^(57,58) As will be shown below, using the modified process flowsheet which consists of only two major steps – fluid-bed calcination⁽⁶⁰⁻⁷³⁾ and hot isostatic press consolidation⁽⁷⁴⁻⁷⁸⁾ – to immobilize neutralized defense waste makes a significant reduction in overall waste management costs compared to the preliminary ceramic process flowsheet.

A. PROCESS MODIFICATIONS

The major process improvements incorporated into the modified ceramic flowsheet are:

- 1) Using fluidized-bed calcination (Figure 1) instead of spray calcination to dry the waste and decompose the metallic compounds to the oxide, fluid-bed calcination produces a relatively high-density⁽⁶⁶⁾ granular product (Figure 2) instead of a low-density powder as formed in spray calcination.⁽⁷⁹⁾ This eliminates dusting and dust separation equipment from the process.
- 2) Vibrapacking the HIP cans instead of tamping to obtain the desired "green density" in the HIP cans.⁽⁶⁶⁾
- 3) Crimp-weld sealing the fill and evacuation tubes on the HIP cans instead of welding a cap on the HIP can and welding the evacuation tube after the HIP can has been outgassed.

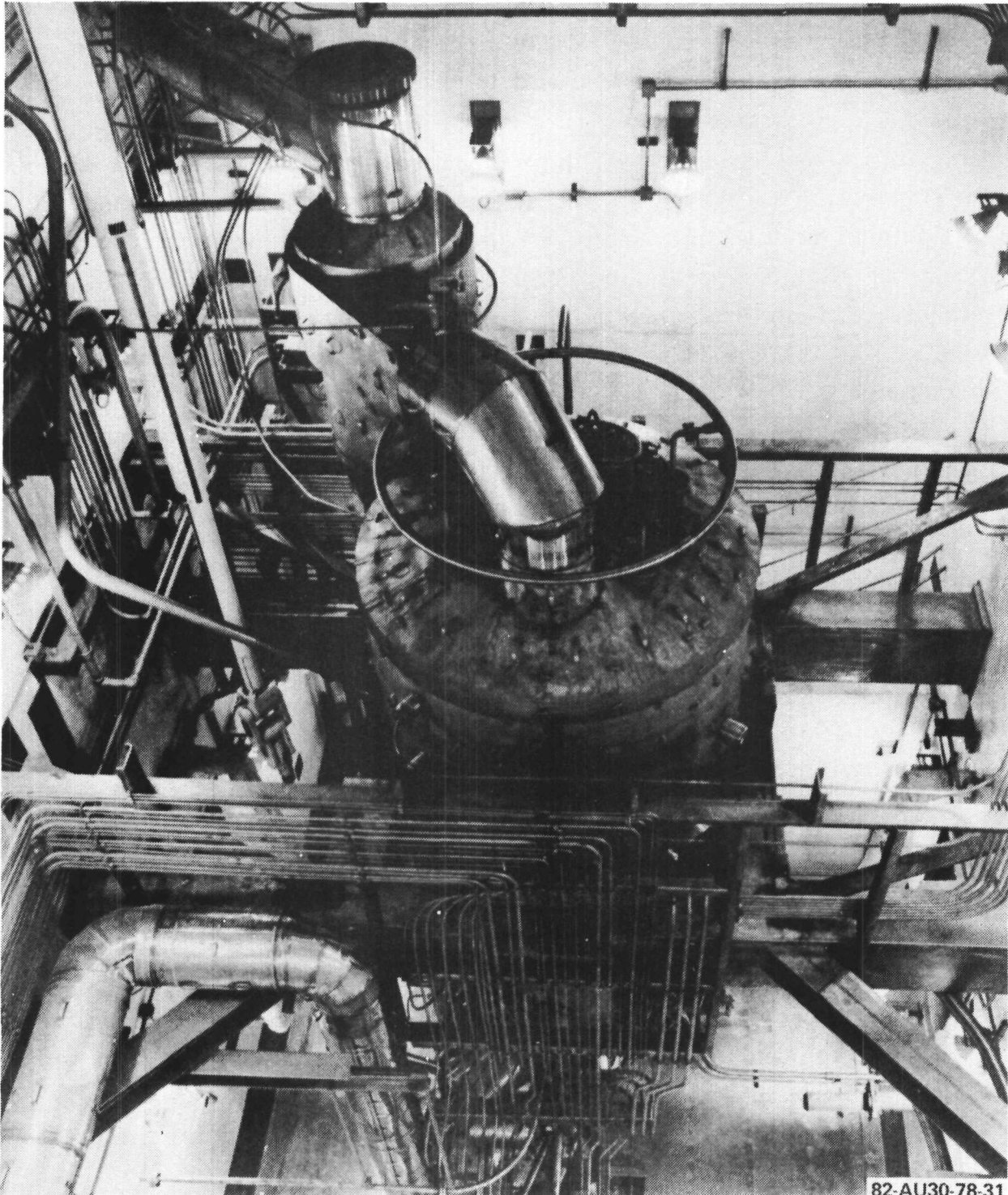
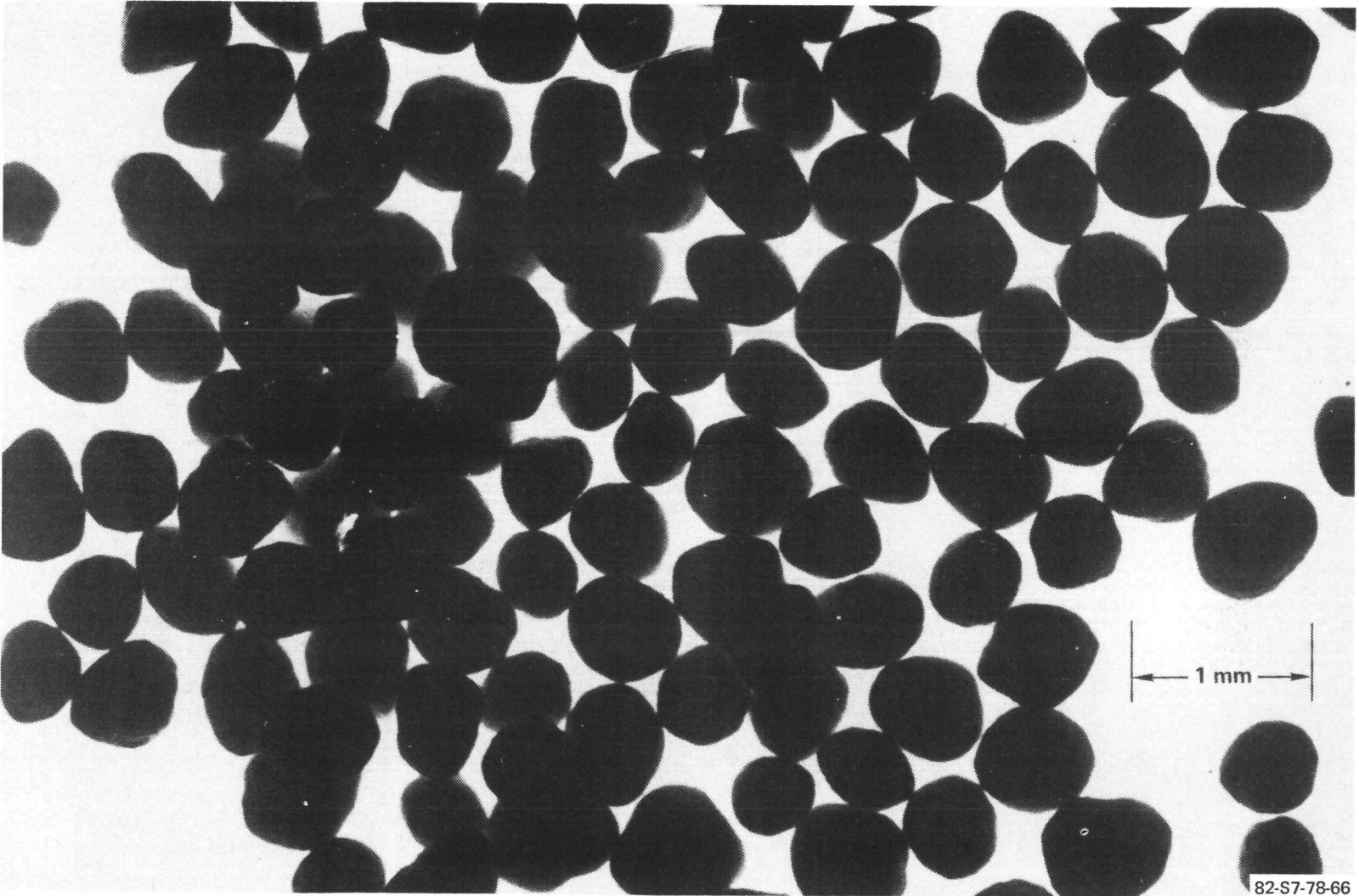


Figure 1. Full-Scale, New High-Level Liquid Waste Calcine Facility at INEL
(Courtesy Exxon Nuclear)

DOE/ET/41900-16
(ESG-DOE-13397)



82-S7-78-66

Figure 2. Simulated Nuclear Waste Fluidized-Bed Calcine Produced from Waste Slurries

- 4) Hot isostatically pressing two or more HIP cans at one time instead of a single can per HIP run.
- 5) Using venturi scrubbers, evaporators, and HEPA filters instead of sand and HEPA filters to decontaminate the off-gas.⁽⁶³⁾
- 6) Using high-pressure water spray jets to decontaminate the HIP cans and canister instead of sandblasting.
- 7) Placing the off-gas processing system after the first decontamination in a separate compartment of the high-level canyon so that if contact maintenance is ever required, it can be performed with minimal decontamination.
- 8) Removing the hot isostatic presses from the processing cell to a separate HIPping cell so that if contact maintenance of the HIP unit is ever required, minimal decontamination would be required.
- 9) Using small regional overhead cranes to move HIP cans during processing instead of relying solely on the large overhead bridge crane for moving cans along the process line.
- 10) Using precalcine tailored waste composition analyses and post-HIP measurements to maintain quality control (QC) of the final waste form. Periodically, a small sample would be HIPped and analyzed to assure quality assurance (QA) specifications and QC methods are adequate.
- 11) Using recanning and re-HIPping to qualify all QC reject forms.
- 12) Eliminating holdup tanks by using filled and sealed HIP cans for surge storage and by installing a redundant HIP unit to assure that HIP cans could be consolidated, canned, and transferred to storage with little, if any, hold up.

In addition to the major changes in the ceramics flowsheet listed above, minor changes were also made. Furthermore, some proposed changes are still being evaluated and may be adopted for use in a future flowsheet. One such proposed change is to wash the larger granules of material, i.e., sand, carbon, and crystallites, and sluice these into HIP cans without milling; this would eliminate the large continuous mill and probably not reduce the quality of the final ceramic waste form for these low-activity particulate components of the waste. An

alternate way of processing these materials would be to screen them from the feed stream and place them in a small ball mill for pulverization. A third way of handling the materials would be to place them in the fluidized bed and let attrition wear them down to the average-sized granules in the fluidized bed.

The calcination method was changed from the spray to the fluid-bed technique to eliminate dusting and produce a granular product that can be vibrapacked to about 50% theoretical green density for reproducible HIP consolidation.⁽⁶⁶⁾ The ~1/2-mm-diameter particles produced in the fluidized-bed calciner (Figure 2) do not dust when transferred and are intrinsically about 90% dense upon formation. Thus, the vibration-packed green density is ~50-60% of theoretical. This permits one to use much smaller HIP cans and other processing equipment. This permitted redesign of the HIPping cans to incorporate tubes for filling and outgassing. These tubes can be crimp-weld sealed. With the redesigned HIP can, the remote grapple and the fill and evacuation fittings can be attached to the can when purchased, thus simplifying processing and improving handleability during processing.

Redesigning the processing and off-gas systems improved operability and substantially reduced costs. Using the HIP cans as surge storage eliminated several surge tanks in the process; this also reduced costs significantly. Changing the method of qualifying QC rejects by recanning and re-HIPping also reduced space requirement. Using small regional overhead cranes to move cans along the line improved productivity.

1. Fluid-Bed Calcination State of the Art

Fluidized-bed calcination has been used to calcine high-level liquid waste for 18 years at the Idaho National Engineering Laboratory (INEL). Although the Waste Calcine Facility (WCF) was designed as a pilot plant,⁽⁶¹⁾ it has been used as a production plant since 1964. Over 1700 m³ (60,000 ft³) of high-level waste calcine has been produced. The \$105 million New Waste Calcine Facility (NWCF) (Figure 1) has undergone cold tests and started calcining high-level waste at INEL in August of 1982.⁽⁶⁰⁾ The NWCF is completely remotely maintained,⁽⁶⁰⁾ whereas the WCF was manually maintained.⁽⁶¹⁾ Therefore, all of the remotization

equipment and procedures required for operating and maintaining high-level liquid waste FBC systems have been developed.⁽⁶⁸⁻⁷³⁾ The WCF, which is 4 ft (1.2 m) in diameter, is about the same size, and the 5-ft (1.5-m) diameter NWCF is larger than a calciner required to process HLLW from a 3000-tonne/year reprocessing plant; i.e., the size of the Barnwell AGNS plant when the second 1500-tonne/year reprocessing line is constructed. One 9-ft-diameter or two 6.5-ft-diameter calciners would be required to process the SRP waste into ceramic forms at the rate of two defense waste canisters of ceramic per day.

Some fluid-bed technology optimization is required for this application. These optimization experiments could be conducted during startup of an actual unit or could be conducted in a small system during construction of an actual fluid-bed system for high-level waste calcination. These optimizations consist of parametric studies to develop process limitations and operating conditions, studies to determine optimum redox control, studies to determine solution/slurry ratio limitations, if any, and studies to determine optimum particle sizes and green densities.

2. Hot Isostatic Pressing State of the Art

Hot isostatic pressing (HIPping) technology has been used in the ceramic, metallurgical, and cement industries⁽⁷⁴⁻⁷⁸⁾ for over 30 years (Figure 3). Over 100 new HIP units are sold annually in the United States. Much larger HIP units are used commercially than would be required to process the calcine from a 3000-tonne/year reprocessing plant. Thousands of forms are HIPped daily with very low rejection rates.⁽⁷⁴⁻⁷⁸⁾ Radioactive materials and spent fuel rods are being consolidated in DOE and commercial HIP units (Figure 4) much larger than required for waste management. Most HIP units are or could be remotely operated; many units are automated so that the entire HIPping operation from loading to unloading is automatic and controlled from a remote console.^(74,75) The HIP pressure vessels are coded, have at least a 20,000-cycle life which exceeds the design life of the facility, and are designed to leak before failure.^(74,75) The waste management HIP consolidation parameters of $\sim 10,000$ psi and $\sim 1100^{\circ}\text{C}$ are moderate compared to many HIPping operations which require up to 30,000 psi or 1500°C .

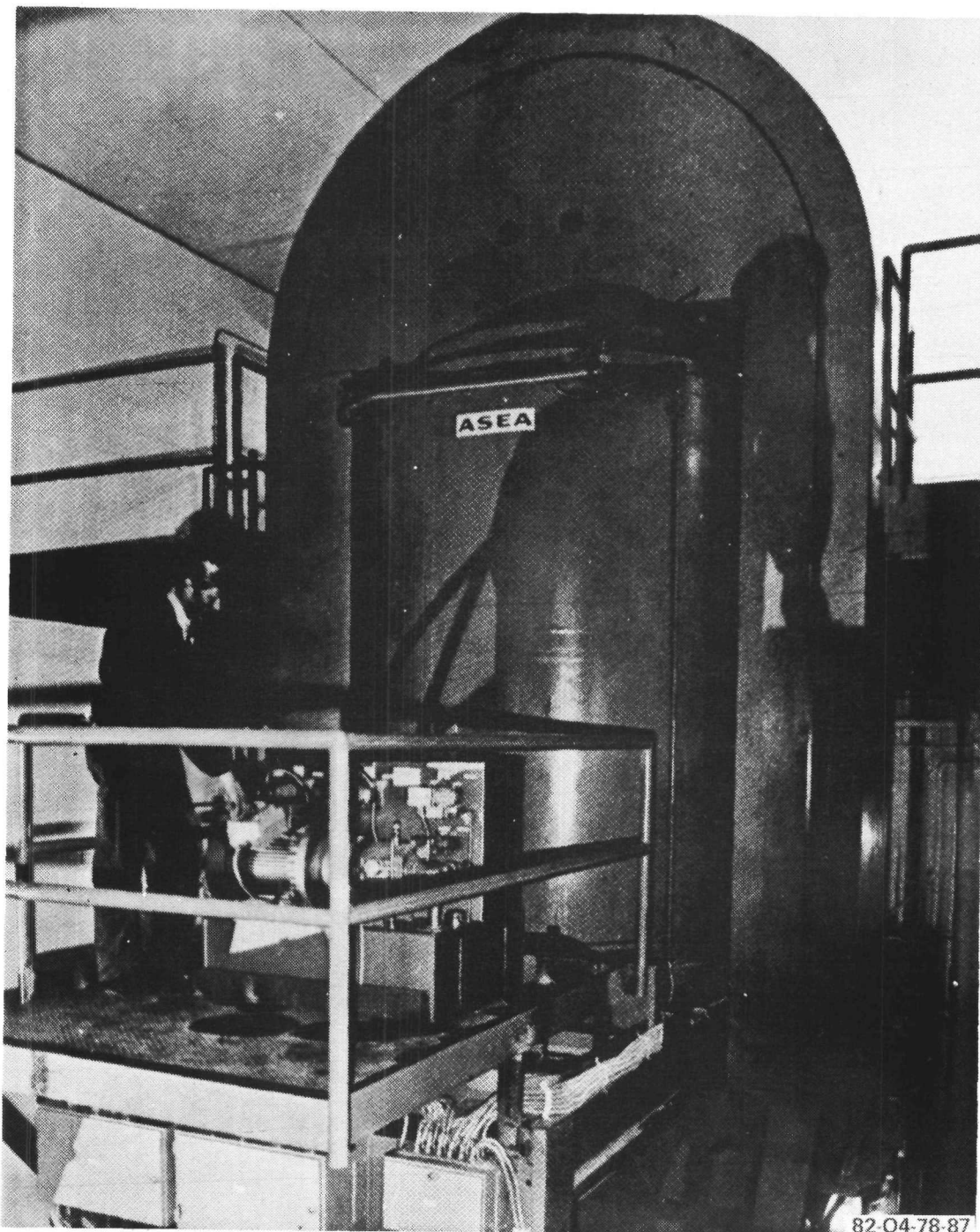


Figure 3. Large HIP Unit Used by ASEA to Encapsulate Spent Fuel Rods in Alumina

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(ESG-DOE-13397)



Figure 4. Encapsulating Simulated Spent Fuel in Ceramic (ASEA)

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(ESG-DOE-13397)

HIP units have two maintenance items: elastomer seals and furnace elements. The elastomer seals must be allowed to degas or be replaced between each run; multiple sealing plates backed by the HIP closure would solve elastomer seal maintenance. The furnace elements, heat shields, and insulation in HIP units usually require replacement about every year; these can be replaced as single units, and for larger HIP units, they are plug-in units and are currently replaced remotely.^(74,75) Thus, HIP technology is well-developed and utilizes technology developed over many years with full-sized systems operated in a radioactive environment.

Some optimization of HIPping technology for this application is also required. Design of a HIP can that would minimize size and cost while maximizing reproducibility would be desirable; although a standard can or a bellows can could be used for this application, neither of these are optimum. Modification of the conventional gasket and furnace replacement techniques and closed-cycle gas recovery systems would optimize these for remote canyon operation and maintenance.

B. MODIFIED CERAMIC FLOW DIAGRAM AND PROCESS LAYOUT FOR NEUTRALIZED DEFENSE WASTE

For comparison, both ceramic and glass canyon layouts were developed to obtain comparative estimates of the capital costs of these two systems. The glass layout was similar to the layout developed for Savannah River⁽⁵⁸⁾ except it was modified to use the same off-gas system and maintenance philosophy as the ceramic process line. These modifications were proposed for the Savannah River glass plant by Rockwell to obtain similar layouts so that more comparative costs would be obtained. Using these modifications reduced the size of the glass plant $\sim 2200 \text{ ft}^2$ compared to the Savannah River glass plant design, but this capital reduction was offset by somewhat greater operating costs than those developed at Savannah River.⁽⁵⁸⁾ Savannah River personnel did not participate in this evaluation and, therefore, some site-specific considerations may alter these costs. However, all major cost items considered by McDonnell⁽⁵⁷⁾ were considered in this study.

The design parameters for the glass and ceramic immobilization systems are given in Table 7. These two systems have the same waste form canister production rate.

TABLE 7
DEFENSE WASTE DESIGN PARAMETERS

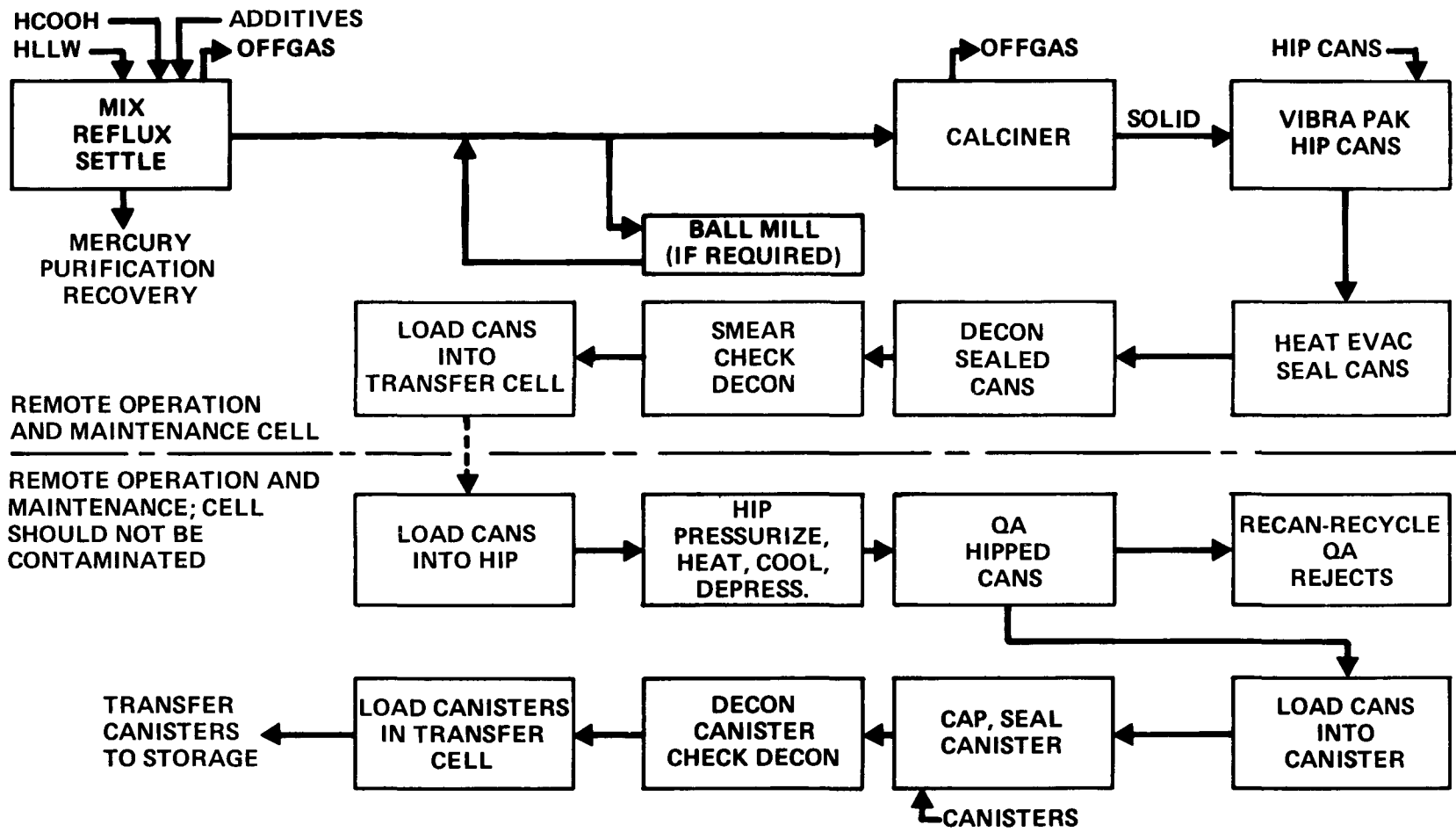
Item	Glass	Ceramic*
Canister production rate (cans/day)	2	2
Processing on-line factor (days/year)	300	300
Product density (g/cm ³)	3.1	4.0
Canister volume (61 cm ID x 300 cm high) (ℓ/can)	876	876
Canister fill factor (%)	76	70
Volume of product per canister (ℓ/can)	666	613
Weight of product (kg/can)	2065	2452
Weight of oxide (glass 25%, ceramic 60%) (kg/can)	516	1471
Weight of additives (kg/can)	1549	985
Heat rate (assumed 400 watts/can for glass) (kW/canister)	0.4	1.14
Sludge composition (kg of waste plus additive oxide equivalent/kg of water)	0.35	0.35
Sludge feed rate		
. kg of waste oxide equivalent/hour	43.0	123
. kg of additive oxide equivalent/hour	129	82
. kg of water/hour	491.4	585

*Modified flow rate to same canister production rate as glass

1. Process Flow Diagram

The ceramic process flow diagram is given in Figure 5. The high-level waste and tailoring additives are mixed with formic acid and refluxed to reduce mercury compounds in the waste to metallic mercury. After settling, the metallic mercury is pumped to a mercury recovery still and the waste-additive mixture is fed to the fluidized-bed calciner. The larger oxide granules are withdrawn from the fluidized bed into the HIP canister and compacted by vibration of the HIP can and connecting tube. The vibrapacked HIP cans are heated, evacuated, and sealed by crimp-welding the fill and evacuation tubes.

DOE/ET/41900-16
 (ESG-DOE-13397)
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Figure 5. Ceramic Preparation Flow Diagram for Neutralized Defense Waste

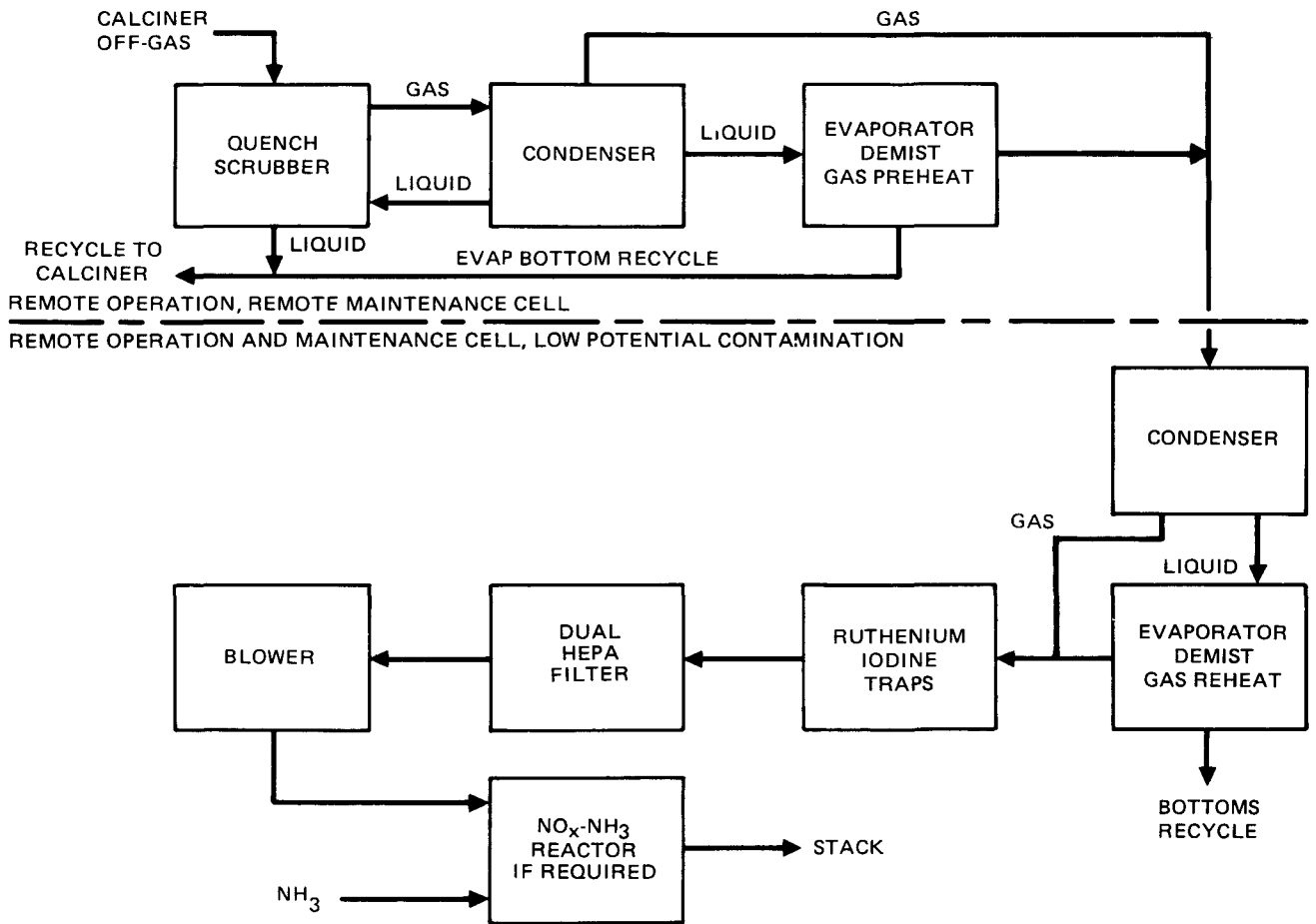
The sealed HIP cans are decontaminated by a high-pressure water spray wash, dried, and smeared to verify decontamination. The decontaminated HIP cans are then transferred to the transfer cell. All activity is sealed within these HIP cans so that subsequent processing will not generate off-gas or allow the spread of contamination.

The HIP cans are transferred to the HIP cell. Two of them are placed into each HIP unit, one above the other. The HIP units are sealed, pressurized to 1.72×10^7 Pa (2500 psi), and heated to 1100°C . The increased temperature causes the HIPping pressure to rise well above the desired 6.89×10^7 Pa (10,000 psi). The cans are maintained at 1100°C and 6.89×10^7 Pa (10,000 psi) for about 15 to 30 min and are allowed to cool. When the temperature reaches $\sim 300^{\circ}\text{C}$, the pressure is released by transferring the argon to the HIP gas recovery tanks and the HIP units are opened. The HIPped cans are transferred to the QA area. Dual HIP units are provided to allow adequate heatup and cooldown times and to assure that no backlog of unHIPped cans builds up, even when one HIP unit is not functioning properly.

The HIPped cans are measured to assure that the required density has been obtained. The cans are then placed three-deep in an external canister which is sealed, decontaminated by a high-pressure water spray, dried, and smeared to assure decontamination. The sealed canisters are then placed in the transfer cell and transferred to storage.

2. Off-Gas Process and Cell Layout

The off-gas from the fluidized-bed calciner is quenched and water-scrubbed. The off-gas then passes through a condenser, an evaporator, a demister, and a gas preheater prior to leaving the high-level canyon (see Figure 6). After the first level of decontamination, the off-gas is transferred to the off-gas processing cell for further decontamination prior to release to the atmosphere. The scrubber slurry is concentrated in the evaporator, and the evaporator still bottoms are returned to the recycle feed tank for subsequent recycle to the calciner.

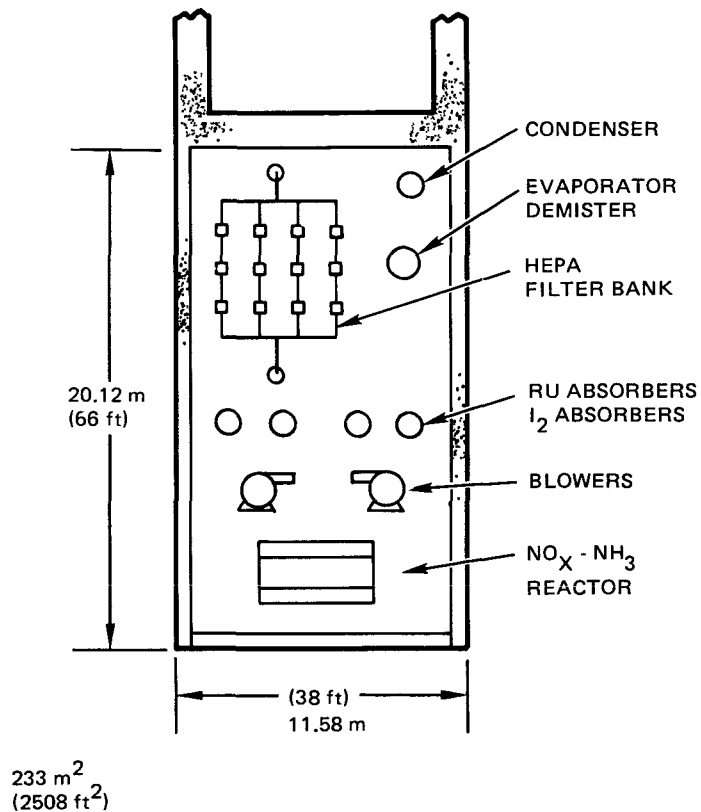


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Figure 6. Flowsheet for Modified Ceramic Process Off-Gas System

In the off-gas processing cell, the off-gas passes through a condenser, an evaporator, a demister, a gas heater, ruthenium and iodine traps, prefilters, and HEPA filters. The decontaminated gas is then forced through a heated, catalyzed NO_x destruction bed, if required, prior to dilution with ventilation air and release to the stack.

The off-gas processing cell layout is shown in Figure 7. The cell is designed so that it can be remotely maintained, but it is anticipated that the level of activity will be low enough for contact maintenance with minimal decontamination if required. Redundant prefilter-HEPA filter systems and blowers are provided to permit continuous operation during maintenance of the other systems. Including the 0.61-m (2 ft) thick concrete shielding, the cell is 20.12 m (66 ft) long by 11.58 m (38 ft) wide or 233 m^2 (2508 ft^2).



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Figure 7. Off-Gas Decontamination Cell

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(ESG-DOE-13397)

3. Process Layout

The dual calciner and dual HIP ceramic process layout for defense waste is given in Figure 8 and consists of five major cells: (1) processing cell, (2) decontamination cell, (3) maintenance cell, (4) HIPping cell, and (5) HIPping gas recovery cell. The overall dimension of the processing canyon with only the first stage of off-gas decontamination is 55.8 m (183 ft) long by 11.6 m (38 ft) wide, including the 1.22-m (4-ft) thick canyon walls, for a total area of 646 m² (6954 ft²). Since the off-gas processing cell contains an additional 233 m² (2508 ft²) for the off-gas system, the net canyon size is 879 m² (9462 ft²).

4. Glass Process Flowsheet and Layout

The glass process flowsheet is similar to the flowsheet developed by Dunson⁽⁵⁸⁾ except that the off-gas processing system shown in Figure 6 was used. The glass process flowsheet is shown in Figure 9, and the process layout is shown in Figure 10. The glass process flowsheet consists of a slurry mix reflux evaporator to reduce the mercury to the metallic state and a mercury recovery system. After mercury reduction, the waste-glass frit mixture is transferred to a melter feed tank and fed to the liquid-fed ceramic melter, where the waste is calcined and mixed with the molten glass. The molten glass containing the radwaste then flows into a canister. Periodically, when the level of the molten glass reached a certain level in the canister, the canister is changed, welded shut, decontaminated, and sent to storage. The glass plant layout shown in Figure 10 is 55.5 m (182 ft) by 11.6 m (38 ft) or 642 m² (6916 ft²) plus the off-gas processing cell for an additional 233 m² (2508 ft²) for a total area of 875 m² (9424 ft²). This is essentially the same size but slightly smaller than the ceramic process layout.

C. NEUTRALIZED DEFENSE WASTE MANAGEMENT COSTS

Defense waste management costs were estimated using a technique similar to that used by McDonnell.⁽⁵⁷⁾ Capital costs of the processing facility were estimated using the $\$455 \times 10^6$ value for a 1093-m³ (11,764-ft²) facility used by McDonnell as a basis and using the 0.6 power factor to adjust these costs to the

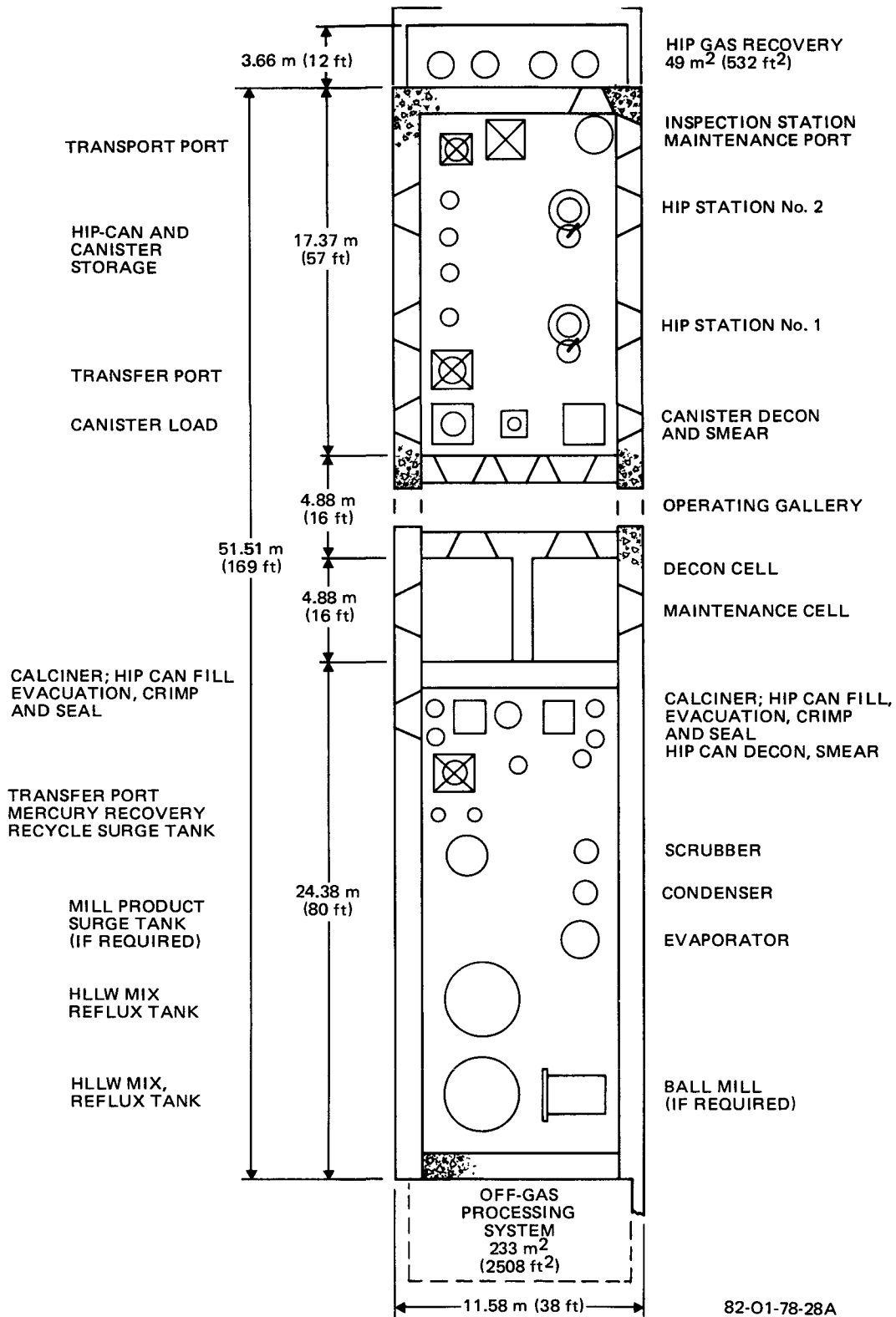


Figure 8. Ceramic Process Layout for Neutralized Defense Waste

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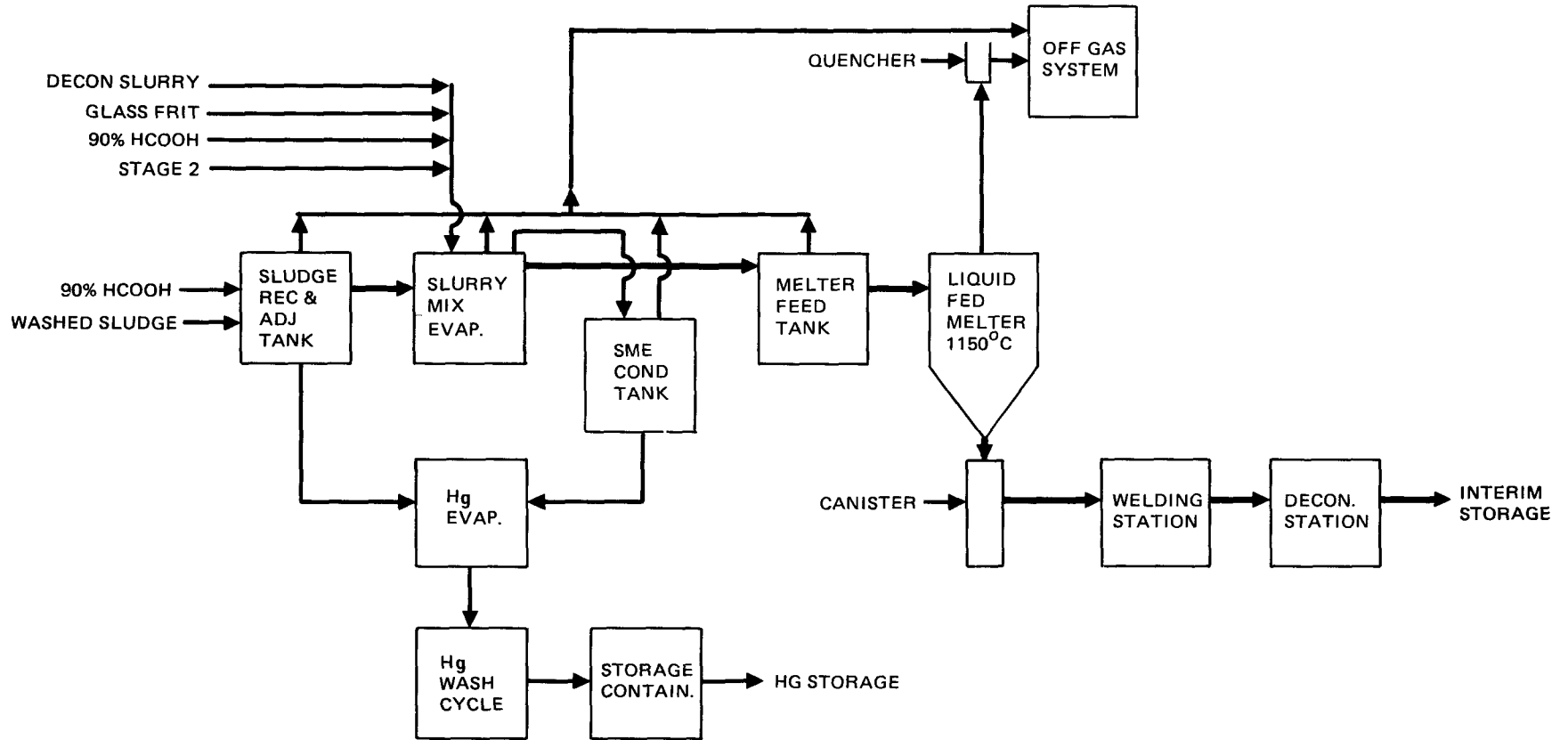
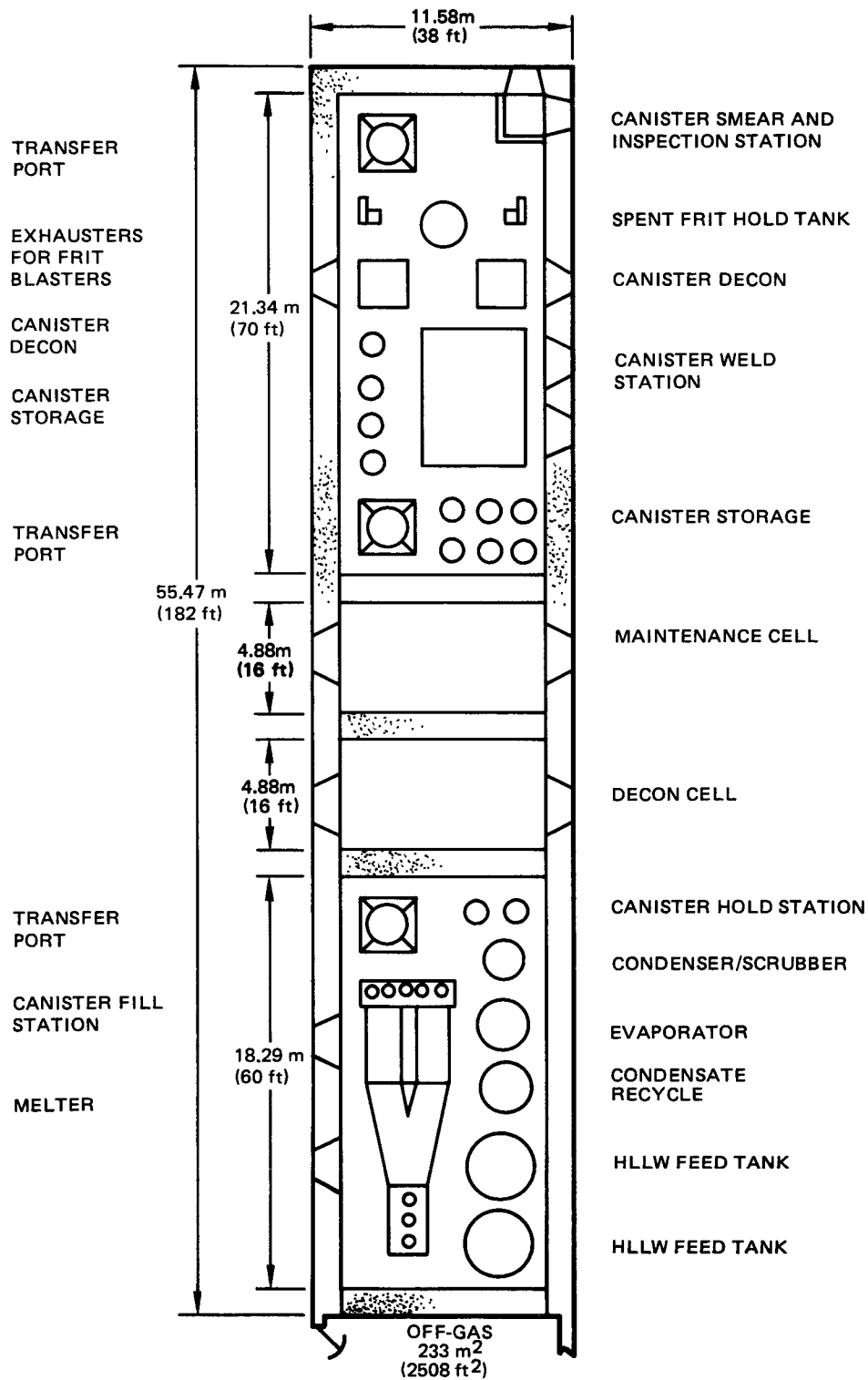


Figure 9. Borosilicate Glass Process Flowsheet



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Figure 10. Layout of Glass Production Canyon for Neutralized Defense Waste

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required size of the process canyons. In addition to these facility costs, lump sums were added for equipment ($\$50 \times 10^6$), the shipping facility ($\$25 \times 10^6$), and the first module of a storage facility ($\$26 \times 10^6$), respectively. The total capital costs of the glass and ceramic waste immobilization facilities are given in Table 8.

Estimated operating costs of the glass and ceramic plants are also given in Table 8. These costs were estimated by assuming a cost of \$80,000/man-year for operations and first-line supervision and engineering. It was assumed that when both lines of the ceramic plant were operating, a crew of 172 (i.e., an average of 43 men/shift) would be required for around-the-clock operation. When one line of the plant was operating, a crew of 125 men (i.e., an average of 31 men/shift) was required. Both ceramic lines would be operated while the current waste inventory was being immobilized (i.e., first 7 years), and only one line would be operated when the subsequently newly produced waste was immobilized. For the glass plant, it was assumed a crew of 145 (i.e., 36 men/shift) were required for glassification of the waste inventory (first 20 years) and a crew of 133 (33 men/shift) would be required to process newly produced waste; i.e., the 3-man crew per shift required to wash the sodium from the waste would not be required when newly produced waste was glassified.

Development costs were estimated at \$65 million for glass⁽⁵⁷⁾ and \$80 million for ceramics. The same tank farm and storage costs as used by McDonnell⁽⁵⁷⁾ were used in this estimate.

Canisters were estimated to cost \$5,500 each, and HIP cans were estimated to cost \$3,000 each. Transportation was estimated to cost \$12,000/canister.⁽⁵⁷⁾

Repository capital costs were obtained from a 72,000-canister repository which was estimated to cost \$2,250 million⁽¹⁾ or \$31,250/canister. The same operating costs, i.e., \$60,500/canister for handling, overpack, and emplacement, were assumed as assumed by McDonnell.⁽⁵⁷⁾

TABLE 8
SRP NEUTRALIZED GOVERNMENT-GENERATED WASTE MANAGEMENT COSTS

	Glass	Ceramics
Size of canisters (in.)	24	24
Number of canisters	10,300	3,400
Costs (\$ millions)		
Immobilization facility capital		
Facility	398	399
Equipment	50	50
Storage	26	26
Shipping	<u>25</u>	<u>25</u>
Total	499	500
Annual operation (During immobilization of current inventory and current production waste)		
Labor	11.6	13.8
Materials	7.8	9.2
Equipment repair	<u>7.5</u>	<u>5.0</u>
Total (annual)	26.9	28.0*
Annual operation (During immobilization of subsequent production after current inventory processed)		
Labor	10.6	10.0
Materials	7.1	6.7
Equipment repair	<u>7.5</u>	<u>5.0</u>
Total (annual)	25.2	21.7*

*If the plant were operated at a constant ceramic production rate so that the current waste inventory plus waste production were processed over the entire 22-year period, operating costs were estimated at $(11.0 + 7.4 + 5.0) \times 10^6$ or $\$23.4 \times 10^6/\text{year}$.

It was assumed that 10,300 canisters of glassified waste or 3,400 canisters of ceramic waste would be produced to immobilize the current waste inventory at Savannah River as well as all newly generated waste produced by the year 2013; these are the canisters of waste reported by McDonnell.⁽⁵⁷⁾ For the ceramic process, the current SRP inventory would be immobilized in 7 years when both processing lines are operating; thereafter, for the next 15 years, only a single line would be operated to immobilize the waste as it is generated at the reprocessing plant. It is assumed that the ceramic process would be fully operational late in 1991. For the glass process, which would become operational in early-1989, 20 years would be required to immobilize the current waste inventory; thereafter, for 5 years, the glass plant would be operated periodically to immobilize high-level waste as it is produced at the reprocessing plant.

As shown in Tables 8 and 9, the immobilization plant capital costs (\$0.57 billion) are the same for glass and ceramic, and the operating costs are virtually the same at \$0.66 and \$0.52 billion for glass and ceramic, respectively. Total waste management costs for Savannah River waste using the glass and ceramic options are given in Table 9 which amount to \$2.5 and \$1.6 billion, respectively. The process layouts considered in this report are not site-specific and site-specific considerations may alter these values. The difference in the cost, \$0.9 billion, arises almost entirely in the repository capital and operating costs.

The DWPF initiative at SRP was launched in 1977, at which time glass was chosen as the reference waste form for SRP high-level wastes. Consequently, large investments have been made in glass development for this application, and all preliminary design investments for the DWPF have been made assuming glass would be the SRP waste form. The costs derived in this report have not considered costs associated with this development work and costs associated with modifying the environmental assessment⁽⁵⁹⁾ and preliminary DWPF design to use ceramics instead of glass. Furthermore, repository cost methodology has not been finalized and, therefore, there can be changes in repository cost allocations. However, it should be pointed out that since only about one-third as many canisters of ceramic require repository emplacement as glass, the ceramic costs are much less sensitive to repository cost changes than glass costs.

TABLE 9
COMPARATIVE WASTE MANAGEMENT COSTS
SRP GOVERNMENT-GENERATED WASTES

	Costs (\$ millions)	
	Glass	Ceramic
Immobilization capital		
Facility	398	399
Facility contingency (17.7%)	70	71
Auxillaries	<u>101</u>	<u>101</u>
Subtotal	569	571
Operating		
Production and inventory (20 yr glass, 7 yr ceramic)	538	196
Production (5 yr glass, 15 yr ceramic)	<u>126</u>	<u>326</u>
Subtotal	664	522
Process development	65	80
Tank farm	9	0
Canisters (\$5,500 ea.)	57	19
HIP cans (\$3,000 ea.)	<u>0</u>	<u>30</u>
Subtotal	57	49
Storage	78	30
Transportation (\$12,000 ea.)	124	41
Repository		
Capital (\$31,250 ea.)	322	106
Operating (\$60,500 ea.)	<u>623</u>	<u>206</u>
Subtotal	<u>945</u>	<u>312</u>
Total waste management costs	2,511	1,605

*Total operating costs were estimated at $\$515 \times 10^6$ if the ceramic plant were operated at a constant waste (current inventory + new production) processing rate over the entire 22-year period.

Lower overall costs using the ceramic option to manage SRP wastes were also found by LLNL.⁽⁸⁰⁾ In this analysis, LLNL reduced the size of the processing canyon designed by DuPont^(57,58) using the original ceramic flowsheet by eliminating the ball mills and one HIP unit and used the (15%) glass contingency for those parts of the processing canyons which were the same (i.e., the auxiliary off-gas processing, feed preparation, and maintenance areas) but used a 35% contingency on those parts of the processing areas that were different for ceramics. Accordingly, LLNL also reduced the ceramic operating costs developed by SRL by eliminating the operating costs associated with the parts of the canyon that were no longer required. In addition, LLNL used more recent tuff⁽⁸⁰⁾ repository costs. With these reductions, the overall waste management costs for Savannah River waste, as derived by LLNL using the ceramic option, was \$2.1 billion⁽⁸⁰⁾ compared with the \$2.9 billion DuPont estimate.⁽⁵⁷⁾

V. DEFENSE AND COMMERCIAL ACID WASTE IMMOBILIZATION AND COSTS

All of the high-level waste in the U.S., except a small volume at West Valley, New York, has been neutralized to permit storage in carbon steel tanks until a waste immobilization process and permanent repository are developed. Eventually, these high-level waste streams will be processed directly without neutralization and storage. Since the high-level waste stream coming from the reprocessing plant is highly acidic ($\sim 2 \text{ M HNO}_3$), a waste immobilization process capable of handling acid wastes will be required. Therefore, an acid HLW ceramic flowsheet and layout were developed.

A. ACID WASTE CERAMIC FLOW DIAGRAM AND PROCESS LAYOUT

1. Design Parameters

The acid waste for a typical Purex 3000-tonne/year reprocessing plant was used for this design.⁽¹⁹⁾ This will be the capacity of the Allied General Nuclear Services (AGNS) plant at Barnwell, South Carolina, when the second 1500-tonne/year processing line is in full operation. The projected waste stream composition from this plant, as described in PNL 3838,⁽¹⁹⁾ was used. Process design criteria are given in Table 10.

2. Fluidized-Bed Calciner

This waste throughput will require approximately a 1.22-m (4-ft) diameter fluidized-bed calciner. This is the size of the water calcine facility at INEL that has operated for 18 years.⁽⁶¹⁾ The calciner consists of four zones. In the first zone, the inert fluidizing gas is heated considerably above the kerosene ignition temperature ($500\text{-}700^\circ\text{C}$) using electrical or fossil-fired heaters. The hot fluidizing gas passes up through the dispersal plate into the second zone of the fluid-bed calciner. This zone of the calciner is $\sim 1.2 \text{ m}$ ($\sim 4 \text{ ft}$) diameter and $\sim 0.31 \text{ m}$ ($\sim 1 \text{ ft}$) tall. In this section, the particles of calcined waste oxide are heated above the autoignition temperature of the fuel ($\sim 385^\circ\text{C}$). At the junction of the second and third zone of the calciner, the high-level liquid acid waste

TABLE 10
 DESIGN VALUES USED FOR GLASS AND CERAMIC PLANTS IMMOBILIZING WASTE FROM
 3000-TONNE/YEAR COMMERCIAL REPROCESSING PLANT

	HLLW		HLLW + ILLW	
	Glass	Ceramic	Glass	Ceramic
Waste oxide production rate (kg/day)	658	658	869	869
Added tailoring agents (kg/day)	1974	439	2607	579
Total oxide (kg/day)	2632	1097	3476	1448
Canister capacity (kg-25 cm canisters)	525	810	525	810
Canister production rate (canisters/day)	5.00	1.35	6.62	1.79
Waste per canister (MTU/canister)	2.0	7.4	1.5	5.6
Heat per canister, 5-year decay (kW/canister)	3.2	12.0	2.4	9.0
Heat per canister, 10-year decay (kW/canister)	1.9	7.2	1.4	5.4
HLLW composition (kg oxide equivalent/kg water)	0.35	0.35	0.35	0.35
HLLW-additive feed rate				
. kg waste oxide equivalent/hour	27	27	36	36
. kg additive oxide equivalent/hour	82	18	109	24
. kg of water/hour	313	131	414	172
Recycle rate				
. kg of oxide/hour	22	9	29	12
. kg of water/hour	63	26	83	35
Calciner feed rate				
. kg of oxide equivalent/hour	132	55	174	72
. kg of water/hour	376	157	497	207
Fluid-bed calciner size				
. m ²		1.28		1.68
. Diameter (cm)		127		146
. Diameter (in.)		50		58
Total volume of gas at condenser exit, 70°C (m ³ /h)		1520		2000
Total volume of gas at filter, 100°C (m ³ /h)		1620		2130
Total area of filter at 0.3 m/sec approach (m ²)		1.5		2.0

mixed with tailoring additives is sprayed onto the fluidized particles of the bed and an auxiliary kerosene heaters are provided to calcine the waste. These particles tend to grow by calcination of the liquid waste on their surfaces in the third section of the calciner. Subsequently, the larger calcined particles settle to the bottom of the calciner by the fluidizing action of the bed. The larger particles are gradually withdrawn from the bed bottom and loaded directly into the HIP can by vibration of the connecting tube and the HIP can receiver (see below). If necessary, a slow gas flow can be drawn through the HIP can to facilitate the transfer of particulates from the calciner to the HIP can. The third, or calcining, zone is somewhat larger in diameter to maintain a constant or slightly reduced upward velocity of the gas as the volume of gas increases due to water vaporization, waste decomposition and combustion, and decreases as the gas cools from the calcining action. This permits smaller particles to grow in this section as the liquid waste dries on the particle surfaces. In the fourth, or deentrainment, zone of the calciner, all but the finest particulates are allowed to settle out of the gas. To facilitate this separation, the diameter of the calciner is increased to reduce the upward velocity of the gas. Finely divided particulates which do not settle out of the gas stream are removed from the gas in the aqueous scrubber and are recycled to the calciner.

3. HIP Cans

A preliminary sketch of the HIP can for commercial high-level waste is shown in Figure 11. Further engineering of this can is required to assure proper design. As currently envisioned, this can is fabricated from low-carbon, low-alloy 40-cm (16-in.) diameter Schedule 5 steel pipe with rounded thin-walled end cap welded on the bottom and a tapered heavy-to-thin-walled cap welded to the top. The heavy-walled center section of the HIP can top end cap has a 2-cm (3/4-in.) diameter fill tube, a 1.3-cm (1/2-in.) diameter evacuation tube connected to a sintered metal filter protruding into the can, and a remote grappler attachment. The HIP can proper is 103 cm (~41 in.) long, with tubes and grappler extending 4.5 cm (~3 in.) more. During HIPping, the can will shrink down to overall dimensions of ~91 cm (36 in.) height and ~28 cm (11 in.) OD. Three of these HIPped cans will fit into the reference canister,^(1,2) which is 30-cm (12-in.) diameter Schedule 40 steel pipe with a height of 3 m (10 ft).

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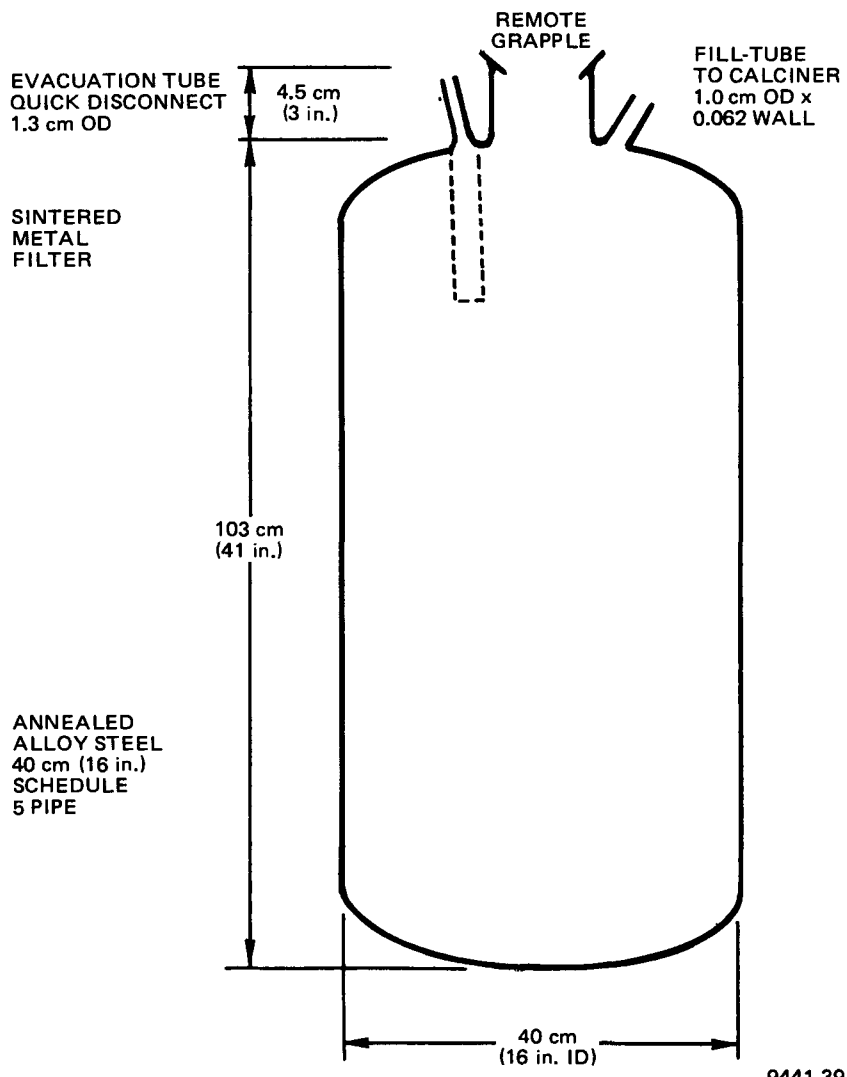


Figure 11. HIPping Can for Commercial Waste

4. Process Flow Diagram

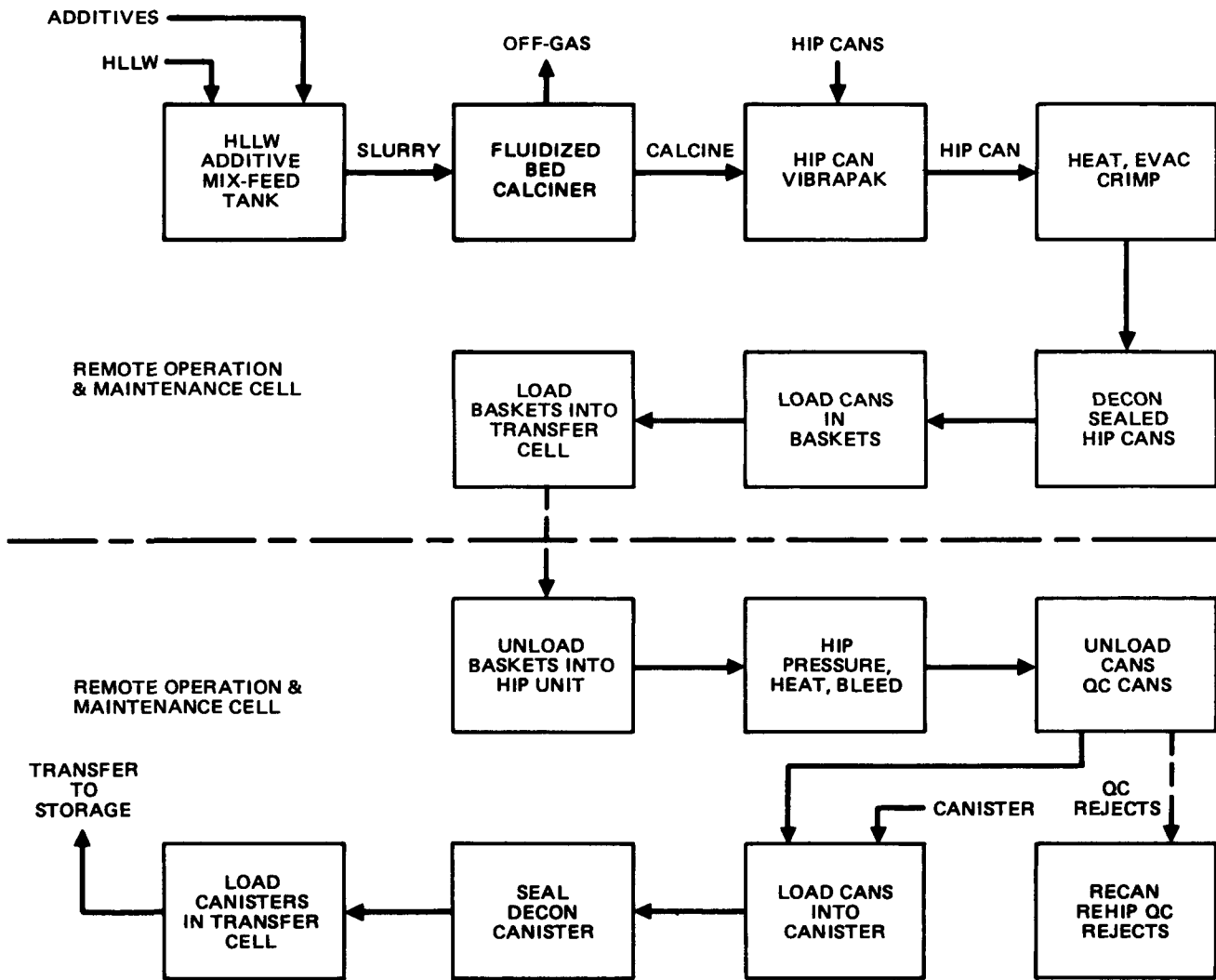
As shown in the acid waste flow diagram (Figure 12), the high-level waste and tailoring additives are mixed directly and fed to the fluidized-bed calciner. The calcine particles are vibrapacked into the HIP cans which are subsequently evacuated, heated, treated with a reducing gas, reevacuated, and crimp-weld sealed. The sealed cans are decontaminated and placed three to a basket and transferred to the HIP cell. The cans are hot isostatically pressed, six at a time, at $\sim 1050^{\circ}\text{C}$ and $\sim 10,000$ psi to assure proper ceramic-phase development. The HIPped cans are checked for QC specifications (primarily density measurement). QC rejects are recanned and reHIPped. Three HIPped cans which meet QA requirements are loaded in the standard canister, which is subsequently capped and welded. The canister is decontaminated and transferred to canister storage. The off-gas system is the same as described earlier for the modified flowsheet for preparing ceramics from neutralized waste (see Figures 6 and 7).

5. Process Layout

The ceramic process layout for acid waste is given in Figure 13 and consists of five major cells: (1) processing cell, (2) decontamination cell, (3) maintenance cell, (4) HIPping cell, and (5) the HIP gas recovery cell. The overall dimensions of the processing canyon are 50.0 m (164 ft) long by 11.6 m (38 ft) wide, including the 1.2-m (4-ft) thick canyon walls, for a total area of 579 m^2 ($6,232\text{ ft}^2$). The off-gas processing layout is identical to that given for the ceramic layout for neutralized defense waste (see Figure 7) and consists of 233 m^2 ($2,508\text{ ft}^2$) for a total area of 812 m^2 ($8,740\text{ ft}^2$).

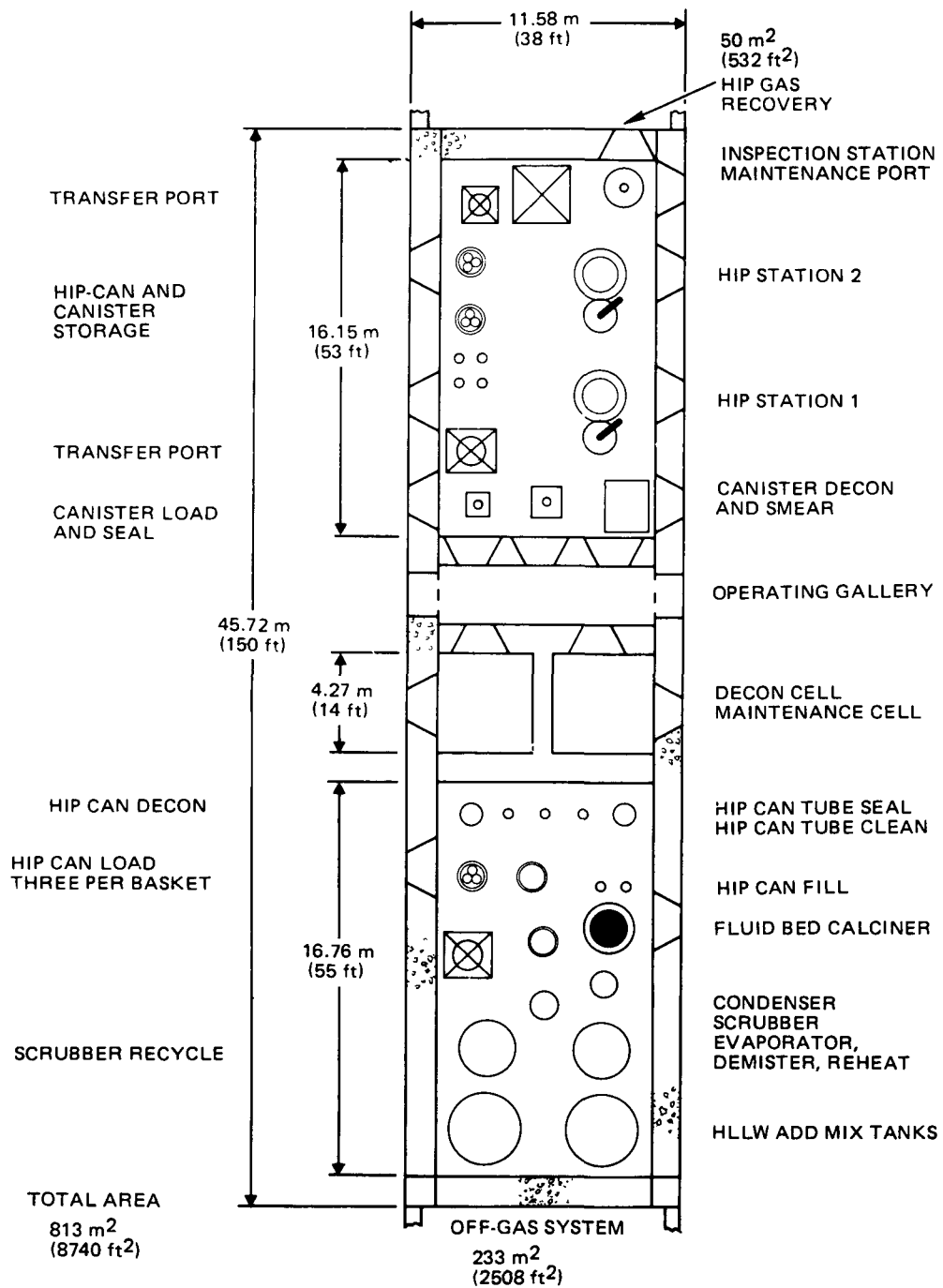
B. ACID WASTE GLASS FLOW DIAGRAM AND PROCESS LAYOUT

An acid waste glass flow diagram and process layout were developed. The process layout shown in Figure 14 consists of a mix tank, melter, canister receiver, transfer cell, and canister sealing decontamination and QA stations. The off-gas from this melting is processed through the off-gas system shown in Figure 7.



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Figure 12. Ceramic Preparation Flow Diagram for Acid Wastes



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Figure 13. Ceramic Process Layout for Acid Waste

DOE/ET/41900-16
(ESG-DOE-13397)

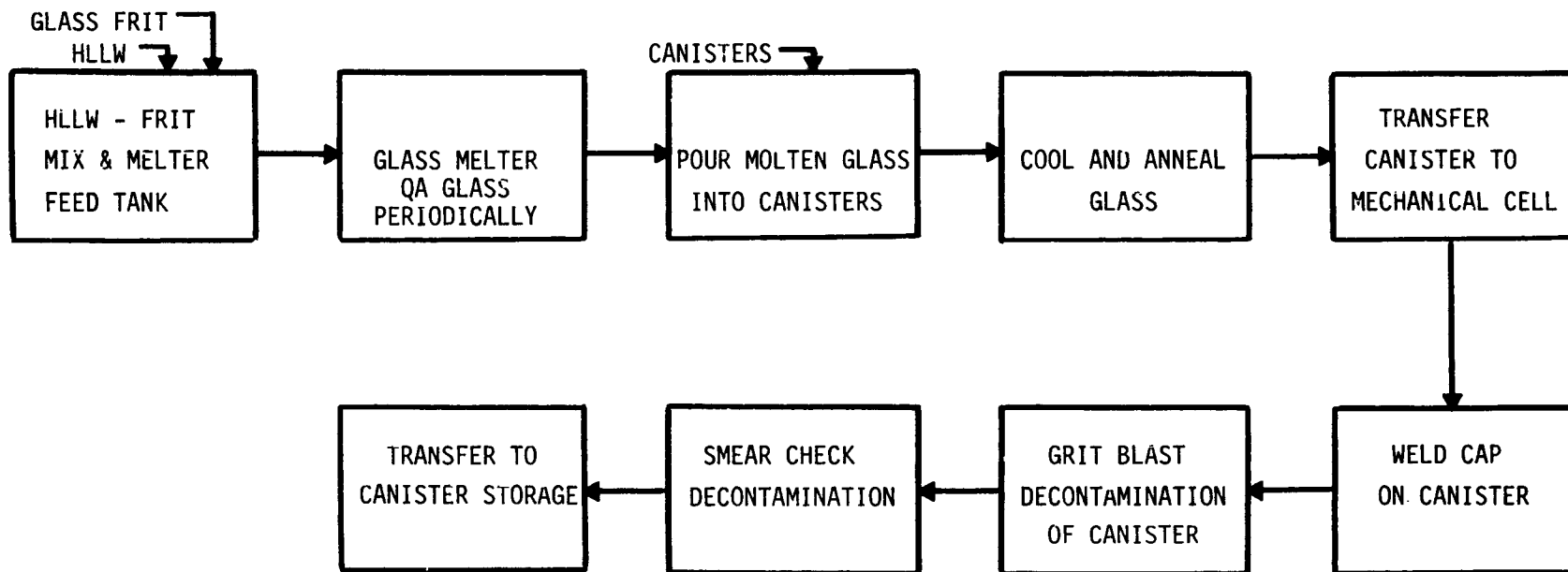


Figure 14. Glass Production Flowsheet for Acid Waste

The acid waste glass process layout is shown in Figure 14. The layout consists of a mechanical cell, a decontamination cell, a maintenance cell, and a melter cell. The overall dimensions are 55.5 m (182 ft) by 11.6 m (38 ft) for a total area of 644 m² (6,916 ft²), including 4-ft-thick canyon walls. The off-gas processing cell as shown in Figure 7 has a total area of 233 m² (2,508 ft²), including the walls, for a total facility area of 877 m² (9,424 ft²).

C. ACID WASTE CERAMIC AND GLASS PLANT PROCESSING COSTS

The comparative glass and ceramic capital and operating costs were determined using the methodology described earlier; namely, the capital cost was determined from the cost of the processing facility developed by McDonnell⁽⁵⁷⁾ using the 0.6 power factor to adjust the cost to the required sized facility.

$$(8,740/11,764)^{0.6} \$455\text{M} = \$381\text{M capital costs of ceramic process cell} \quad (4)$$

$$(9,424/11,764)^{0.6} \$455\text{M} = \$398\text{M capital costs of glass process cell} \quad (5)$$

Total capital costs of the ceramic facility consist of the cell costs (Equation 4), equipment costs of \$50M, shipping facility of \$25M, and storage facility of \$26M for a total of \$482M. Total capital costs for the glass facility consist of the cell costs (Equation 5), equipment costs of \$50M, shipping and storage costs of \$25M and \$26M, respectively, for a total of \$499M.

Operating costs were calculated as described previously in Section IV.D and in detail in Reference 52. The four-shift crew to operate the ceramic and glass plants required 122 and 133 men, respectively. Therefore, the total labor costs for the ceramic and glass plants, respectively, were \$10.0M/year and \$10.6M/year, respectively. Materials and supplies for the ceramic and glass plants were \$6.7M/year and \$7.1M/year, respectively. Annual capital equipment replacement costs for the ceramic and glass plants were \$5.0 and \$7.5M/year. Thus, the total annual operating cost for the ceramic was \$21.7M/year, and the total annual

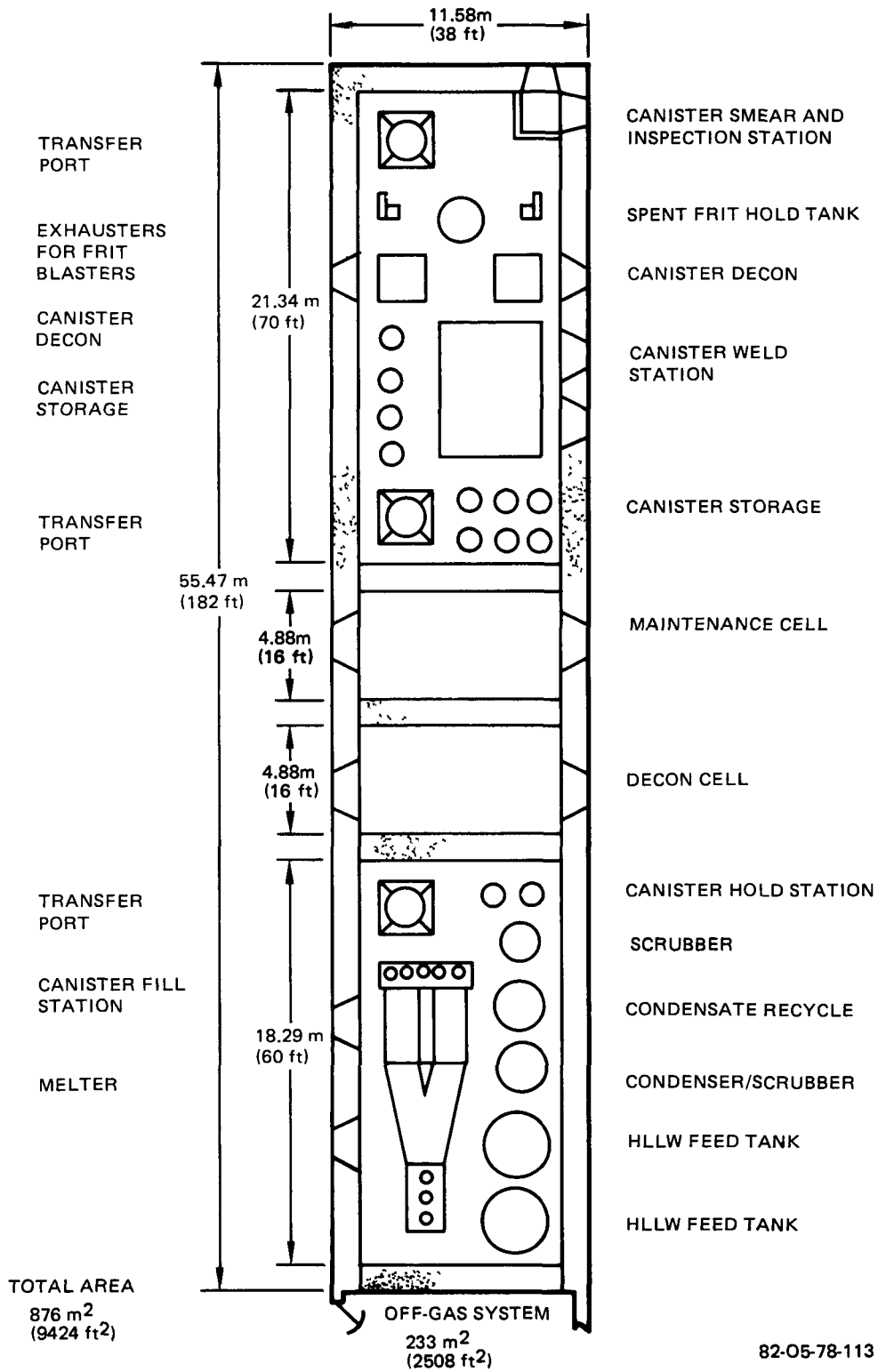


Figure 15. Layout of Glass Production Canyon for Commercial (Acid) Waste

DOE/ET/41900-16
(ESG-DOE-13397)

operating cost for the glass plant was \$25.2M/year. These costs are summarized in Table 11. Thus, with this costing methodology, the capital and operating costs of the glass and ceramic plants are about 3% (\$17M) apart. The difference in the annual operating costs is about 14% (\$3.5M). Thus, for commercial acid waste management, the differences between the capital and operating costs for the ceramic and glass immobilization processes are small. If operating costs for a 20-year period are considered, then the difference in total capital and operating costs for the ceramic and glass is only about \$87M or <10%. This is within the error in the estimates. So for all practical purposes, the total capital and operating costs for either the ceramic or glass processing plant are the same. In addition to these costs, the remainder of the waste management cost must be added to obtain total waste management cost. The differential total commercial waste management costs are discussed by McKisson⁽⁵²⁾ in a companion report where it is shown that the ceramic waste management option can be more cost effective.

TABLE 11
SUMMARY OF ACID WASTE IMMOBILIZATION PLANT
CAPITAL AND OPERATING COSTS

Cost Type	Costs (Millions of 1981 dollars)	
	Ceramic	Glass
Capital		
Processing facility	381	398
Equipment	50	50
Storage facility	26	26
Shipping facility	<u>25</u>	<u>25</u>
Total	482	499
Operating (Annual)		
Labor	10.0	10.6
Materials and supplies	6.7	7.1
Equipment replacement	<u>5.0</u>	<u>7.5</u>
Total	21.7	25.2
20-year operating costs	434	504

DOE/ET/41900-16
(ESG-DOE-13397)

VI. CERAMIC PLANT FOR HANFORD WASTE AND OTHER HIGH-LEVEL WASTES

At some reprocessing sites, an immobilization plant readily adaptable to either acid or neutralized waste streams will be required. For example, at the Hanford reprocessing plant, the defense waste will be neutralized until after an immobilization plant can be built and some of the neutralized backlog has been processed (~1990). Thereafter, the immobilization plant will process both freshly generated neutralized and acid waste. Eventually, other spent fuels with much higher burnups and much higher transuranic content, such as the Fast Flux Test Reactor fuel, may also be processed at Hanford. Waste streams from the reprocessing of this fuel would probably have significantly different compositions with higher heat content than current waste streams from reprocessing. The higher thermal stability of ceramics and its great flexibility in accepting waste streams of widely varying compositions make it ideal for immobilizing the variety of waste streams that might be produced at Hanford. Furthermore, the compactness of the ceramic processing components and modularizability of the processing operations may permit the installation of a full-scale ceramic plant in the existing Hanford Waste Management Facility.

The Hanford Waste Management Facility cells are approximately 18 ft deep by 13 ft wide by 21 ft high. A few of these cells might be dedicated to a ceramic process waste immobilization system. These cells may be adequate in size to accommodate a full-scale ceramic plant but might not accommodate a full-scale glass plant without major modifications due to the large size of the melter. Due to recent advances in ceramic process development, a ceramics plant might be installed and operating at Hanford using the existing Waste Management Facility before a new facility could be built to accommodate a full-scale glass plant. This, plus the fact that ceramics produce a superior product for less overall cost, should make a ceramic plant a candidate for waste immobilization at Hanford.

A small amount of high-level liquid waste exists at West Valley, New York. The applicability of the ceramic process to widely varying waste streams including high sodium wastes as well as the smallness and modularizability of the process components suggests that this method of processing these wastes should be

considered. It may be possible to retrofit a ceramic processing line into the existing processing facility; this may save a considerable amount of money and time in decontaminating and decommissioning this facility. In addition, a superior, more leach-resistant waste form should result; the lower number of ceramic waste forms required for immobilization of the West Valley should substantially reduce transportation, storage, and repository costs.

The superior leach resistance of actinides from ceramics suggests that this method of managing TRU wastes should be considered. The long-lived actinides and their daughter products constitute a hazard to man if they are not effectively isolated from the biosphere for a million years or more. The natural evidence of mineral stability in geologic leaching environments suggests that these nuclides could be effectively immobilized in the ceramic waste form itself without relying on the repository or other engineered barriers to prevent contamination of the biosphere. This would provide another safety factor readily translated into terms the public could understand; i.e., "return the nuclides back to the earth in the stable mineral form in which they occur naturally." Thus, the ceramic method of managing these wastes should be considered.

VII. CONCLUSIONS AND RECOMMENDATIONS

Ceramic waste forms have the same or similar crystalline phases as naturally occurring minerals. Since these minerals have existed in a geologic environment for millions of years, there is every reason to believe that mineral analogues containing radionuclides will resist dissolution in geologic environments for similar periods of time. Acceptance of the long-term isolation of nuclear waste will have to result from mathematical models based on firm technical data on the predicted behavior of materials for long periods of time. Relating the behavior of ceramic waste forms to that of natural minerals provides an additional avenue for developing this technical data base.

Ceramic waste forms have desirable chemical and physical properties such as thermal stability, thermal conductivity, and leach resistance. For the actinides, which are the source of most of the long-lived radionuclides which present a hazard to man if they enter the biosphere,⁽⁴⁷⁻⁴⁹⁾ the ceramic waste forms are about two to three orders of magnitude more leach resistant than glass.^(41,42) When the basic ceramic waste form matrix material, alumina and titania, is compared to the basic glass matrix, silica, the ceramic matrices are again more leach resistant and, therefore, will maintain the waste form integrity better as crystalline ceramics than as glass, particularly under hydrothermal leach conditions.⁽⁴¹⁾ Ceramics do not devitrify and they provide a greater flexibility of waste management options than glass. The impact resistance of ceramics would probably provide comparatively better radioactive retention performance in the event of an accident.

The higher waste loading (up to 90 wt. %) and density (up to 5.6 g/cm^3) of ceramic nuclear waste forms provide many waste management options not available to the borosilicate glass reference waste form, which is limited to densities of about 3.2 g/cm^3 and waste loadings of about 35 wt. % to avoid separate phase formation during vitrification. Ceramics incorporate the radionuclides in the crystalline structure, while glass encapsulates the radionuclides as tiny crystallites or solutes in otherwise solid vitreous material. Thus, it is not surprising that ceramics exhibit superior thermal stability and hydrothermal leach-resistant

properties;^(41,42) these superior properties allow additional options for more cost-effective waste management.

Assuming safety criteria are satisfied, nuclear waste management system analyses should consider volume reduction or waste loading as independent variables in order to minimize overall waste management costs. Ceramic waste forms with up to 90 wt. % waste loading and densities of up to 5.6 g/cm^3 offer a much broader economic optimization potential than does glass, which can accommodate waste loadings only up to ~ 35 wt. % and densities only up to $\sim 3.2 \text{ g/cm}^3$.

Preliminary process flow diagrams and process layouts suggest that a ceramic immobilization process could be designed to process both neutralized and acid high-level liquid wastes from commercial or Government reprocessing plants. Ceramics have great flexibility in accepting variable waste feed compositions. There appear to be other processing, operating, and maintenance advantages of the ceramic process such as avoiding molten materials and reducing corrosion and contamination of the processing cells.

Preliminary comparative cost analyses of ceramic and glass waste management options suggests that ceramics may be cost effective in the permanent disposal of the waste in the repository. Using our base design, Savannah River defense waste management costs are $\sim \$0.9$ billion less for ceramics than glass. This cost advantage is sensitive to repository cost allocations which are still undetermined. However, whatever decisions are made for repository cost allocations, the ceramic option is less dependent on these future decisions because of its capacity for high waste loading.

DuPont developed the first cost estimate of \$2.9 billion for ceramic management of SRP waste.⁽⁵⁷⁾ LLNL reduced this estimate to \$2.1 billion by reallocating contingencies and repository costs.⁽⁸⁰⁾ This study reduced these costs to \$1.6 billion by redesigning the ceramic plant and by reducing the contingency further because of full-scale demonstration of process steps. This study is not site-specific and site-specific considerations may alter these costs somewhat.

The flexibility of the ceramics process to accommodate widely varying waste compositions and waste thermal loadings, as well as the process' adaptability to modularization, makes the ceramics process a candidate for immobilization of Hanford and NFS Purex waste. Essentially, a full-scale ceramics process can be retrofitted into the existing waste management cells; whereas only a part-scale glass plant can be accommodated. This, plus the fact that a superior waste form can be produced at potentially lower overall costs as well as the fact that substantially fewer ceramic waste canisters would be produced and would require storage until the repository is ready, suggests that the ceramic waste form should be evaluated for these wastes. Management of TRU wastes using the ceramic option should be evaluated further due to the greater leach resistance of actinides from the ceramic waste forms.

It is concluded from this and other studies that the ceramic waste form may offer important advantages over glass in leach resistance, waste loading, density, and process flexibility. In addition, preliminary economic calculations indicate that ceramics must be considered a leading candidate for the form to immobilize high-level wastes. Continued development of ceramics for this purpose is consequently warranted and recommended.

VIII. REFERENCES

1. Staff, Westinghouse Advanced Energy Systems Division, "Engineered Waste Package Design, Defense High Level Waste (Form 1), Commercial High Level Waste (Form 1) and Spent Fuel (Form 2) Disposal in Basalt," AESD-TME-3113 (draft) (September 1981)
2. Staff, Westinghouse Advanced Energy Systems Division, "Engineered Waste Package Design, Defense High Level Waste (Form 1), Commercial High Level Waste (Form 1) and Spent Fuel (Form 2) Disposal in Salt," AESD-TME-3131 (draft) (November 1981)
3. C. Klingsberg and D. Duguid, "Isolating Radioactive Waste — The Multibarrier Concept May Be the Key to Safe Disposal," Amer. Scientist 70, 182 (1982)
4. S. Gonzales, "Host Rock for Radioactive Waste Disposal," Amer. Scientist 70, 191 (1982)
5. "Management of Commercially Generated Radioactive Waste," Final Environmental Impact Statement, Volumes 1, 2, and 3, DOE/EIS-0046F (October 1980)
6. "Defense Waste Processing Facility, Savannah River Plant, Aiken, S.C.," draft Environmental Impact Statement, U.S. Department of Energy, DOE/EIS-00820 (September 1981)
7. T. A. Bernadzikowski et al., "The Evaluation and Selection of Candidate High Level Waste Forms," DOE/TIC-11611 (February 1982)
8. L. M. Papouchado et al., "Small Scale Processing of Actual Savannah River High Level Waste," Amer. Nucl. Soc. Trans. 39, 171 (1981)
9. G. B. Woolsey and M. J. Plodinec, "Vitrification of High-Level Radioactive Waste in a Small-Scale Joule-Heated Ceramic Melter," Scientific Basis for Nuclear Waste Management, 4, Plenum Press, New York (1979)
10. R. G. Baxter, "Description of DWPF Reference Waste Form and Canister," DP-1606 (June 1981)
11. J. L. Butler et al., "Description of Ceramic Waste Form and Canister for Savannah River Plant Waste," DP-1626 (1982)
12. D. E. Larson, ed., "Spray Calcliner/In-Can Melter High-Level Waste Solidification Technical Manual," PNL-3495 (1980)
13. J. E. Mendel and J. L. McElroy, "Waste Solidification Program: Volume 10, Evaluation of Solidified Waste Products," BNWL-1666 (1972)
14. J. E. Mendel, "The Storage and Disposal of Radioactive Waste as Glass in Canisters," PNL- 2764 (1978)

DOE/ET/41900-16
(ESG-DOE-13397)

15. W. F. Merritt, "High-Level Waste Glass: Field Leach Test," Nuclear Tech. 32, 88-91 (1977)
16. W. A. Ross et al., "Annual Report on the Characterization of High-Level Waste Glasses," PNL-2625 (1978)
17. R. A. Ross et al., "Annual Report on the Development and Characterization of Solidified Forms for High-Level Wastes, 1978," PNL-3060 (1979)
18. Staff, U.S. Department of Energy, "Technology for Commercial Radioactive Waste Management," DOE/ET-0028 (1979)
19. S. C. Slate et al., "Reference Commercial High-Level Waste Glass and Canister Definition," PNL-3838 (September 1981)
20. J. E. Mendel et al., "Annual Report on the Characteristics of High Level Waste Glasses," BNWL-2252 (June 1977)
21. G. J. McCarthy, "High Level Waste Ceramics: Material Considerations, Process Simulation, and Product Characterizations," Nuclear Tech. 32, pp 92-105 (1977)
22. G. J. McCarthy, "High Level Waste Ceramics," Trans. Am. Nucl. Soc. 23, pp 168-180 (1976)
23. R. Roy, "Rational Molecular Engineering of Ceramic Materials," J. Am. Ceram. Soc. 60, pp 350-363 (1977)
24. G. J. McCarthy et al., "Interactions Between Nuclear Waste and Surrounding Rock," Nature 273, pp 217-219 (1978)
25. A. E. Ringwood et al., "The Synroc Process: A Geochemical Approach to Nuclear Waste Immobilization," Geochemical Journal 13, pp 141-165 (1979)
26. A. E. Ringwood et al., "Immobilization of High Level Nuclear Reactor Wastes in Synroc," Nature 278, pp 219-223 (March 1979)
27. A. E. Ringwood, "Immobilization of Radioactive Wastes in Synroc," Amer. Scientist 70, 201 (1982)
28. P. E. D. Morgan et al., "The Magnetoplumbite Crystal Structure as a Rad-waste Host," J. Amer. Ceram. Soc. 65, C114 (1982)
29. C. Hoenig et al., "Preparation and Properties of Synroc D Containing Simulated Savannah River Plant Wastes," UCRL-53195 (July 1981)
30. J. H. Campbell et al., "Immobilization of High Level Defense Waste in Synroc-D: Recent Research and Development Results on Process Scale-Up, Treatment and Handling of Radioactive Wastes Meeting, Richland, Washington, page 324, Battelle Press (April 1982)

31. A. B. Harker et al., "Tailored Ceramic Nuclear Waste Forms: Preparation and Characterization," Proc. International Symp. on Scientific Basis for Nuclear Waste Management, Boston, Massachusetts (November 1980)
32. A. B. Harker et al., "Formulation and Processing of Polyphase Ceramics for High-Level Nuclear Waste," Scientific Basis for Nuclear Waste Management, 6, 567, Plenum Press, New York (1982)
33. A. B. Harker et al., "An Improved Polyphase Ceramic for High-Level Defense Waste," Proceedings of the ANS Topical Meeting on the Treatment and Handling of Radioactive Wastes, Battelle Press, page 335 (April 1982)
34. C. M. Jantzen et al., "The Leaching of Tailored Polyphase Nuclear Waste Ceramics: Microstructural and Phase Characterization," J. Am. Ceram. Soc. (1982) (in press)
35. J. Campbell et al., "Properties of Synroc-D Nuclear Waste Form: A State-of-the-Art Review," UCRL-53240, Lawrence Livermore National Laboratory (January 1982)
36. H. Curien et al., "Hibonite, A New Mineral Species," Compt. Rend. 242, 2845 (1956)
37. P. E. D. Morgan, "Unique Host Sites of Magnetoplumbite," Bull. Amer. Ceram. Soc. 59, p 397 (1980)
38. L. F. Grantham and J. F. Flintoff, "High Nuclear Waste Loading in Tailored Ceramics," Proc. of the Symposium on High Temp. Materials Chemistry, D. D. Cubicciotti and D. L. Hildenbrand, editors, 82-1, page 162, Elec. Chem. Soc. (1982)
39. L. F. Grantham and J. F. Flintoff, "Spray Calcination of SRP Waste Compositions for Ceramic Waste Forms," Treatment and Handling of Radioactive Waste Meeting, Richland, Washington, Battelle Press, page 445 (April 1982)
40. C. M. Jantzen et al., "Ceramic Nuclear Waste Forms," Proceedings of the International Seminar in Chemistry and Process Engineering for High Level Liquid Waste Solidification, Julich, West Germany (1981)
41. A. B. Harker et al., "Waste Form Development and Characterization," DOE document in press (~February 1983)
42. J. A. Stone et al., "Comparison of Properties of Borosilicate Glass and Crystalline Waste Forms for Immobilization of Savannah River Wastes," DP-1627 (April 1982)
43. "Geological Criteria for Repositories for High-Level Radioactive Wastes," Panel on Geological Site Criteria, National Academy of Sciences, Washington, D.C. (August 3, 1978)

44. B. Gilletti et al., "State of Geological Knowledge Regarding Potential Transport of High-Level Radioactive Waste From Deep Continental Repositories," EPA/520/4-78-004, U.S. EPA, Washington, D.C. (June 1978)
45. M. J. Smith et al., "Engineered Barrier Development for a Nuclear Waste Repository in Basalt: An Integration of Current Knowledge," RHO-BWI-ST-7, Rockwell Hanford Operations, Richland, Washington (May 1980)
46. C. Klingsberg and J. Duguid, "Status of Technology for Isolating High-Level Radioactive Wastes in Geologic Repositories," DOE/TIC-11207, U.S. DOE (draft) (October 1980)
47. G. S. Barney and B. J. Wood, "Identification of Key Radionuclides in a Nuclear Waste Repository in Basalt," RHO-BWI-ST-9, Rockwell Hanford Operations, Richland, Washington (May 1980)
48. T. H. Pigford, "Geological Disposal of Radioactive Waste," Chemical Engineering Progress, pp 18-26 (March 1982)
49. T. H. Pigford et al., "Migration of Radionuclides Through Sorbing Media: Analytical Solutions-II," LBL-11616, Vol I and II (October 1980)
50. "Draft Environmental Impact Statement - Management of Commercially Generated Radioactive Waste," DOE/EIS-04460, Vol 2, Appendix P (1979)
51. L. P. Hatch, "Ultimate Disposal of Radioactive Wastes," Am. Sci., 41, 410-21 (1953)
52. R. L. McKisson et al., "Commercial High Level Waste Management Options and Economics - A Comparative Analysis of the Ceramic and Glass Waste Forms," DOE document in press (~February 1983)
53. G. J. McCarthy, "Quartz-Matrix Isolation of Radioactive Wastes," J. Material Sci., 8, 1358-59 (1973)
54. R. Roy, "Rational Molecular Engineering of Ceramic Materials," J. Am. Ceram. Soc. 60 (7-8), 350-63 (1977)
55. P. E. D. Morgan et al., "High-Alumina Tailored Nuclear Waste Ceramics," J. Am. Ceram. Soc. 64 (5), 249-258 (1981)
56. "The Evaluation and Review of Alternate Waste Forms for Immobilization of High-Level Radioactive Wastes," No. 3, DOE/TIC-11472, The Alternate Waste Form Peer Review Panel (July 1, 1981)
57. W. R. McDonell, "Comparison of SRP High-Level Waste Disposal Costs for Borosilicate Glass and Crystalline Ceramic Waste Forms," DPST-82-346 (April 1982)
58. J. B. Dunson et al., "Assessment of Processes, Facilities and Costs for Alternative Solid Form for Immobilization of SRP Defense Waste," DP-1625 (April 1982)

DOE/ET/41900-16
(ESG-DOE-13397)

59. "Environmental Assessment, Waste Form Selection for SRP High-Level Waste," DOE/EA-0179 (July 1982)
60. R. R. Smith, G. E. Bingham, and F. D. Bench, "The New Waste Calcining Facility at ICPP," Proc. of the Amer. Nuc. Soc. Topical Meeting on the Treatment and Handling of Radioactive Waste, p 455, Battelle Press (April 1982)
61. J. Berreth and B. R. Dickey, "High Level Waste Management at the Idaho Chemical Processing Plant," Proc. of the Amer. Nuc. Soc. Topical Meeting on the Treatment and Handling of Radioactive Waste, p 449, Battelle Press (April 1982)
62. J. T. Nichols, "ICPP Development Programs for Fluidized-Bed Calciner Heat Input," ICPP-1169 (September 1978)
63. W. A. Freeby, "Off-Gas Cleanup System Considerations for Fluidized-Bed Radioactive Waste Calcination at the ICPP," ICPP-1162 (August 1978)
64. E. S. Grimmett and D. H. Munger, "Product Removal and Solids Transport from Fluidized-Bed Calciners," ICPP-1161 (September 1978)
65. J. A. Hendricks and A. G. Westra, "A Prototype Facility to Demonstrate Retrieval of Simulated ICPP Calcine Waste," INICO-1093 (September 1981)
66. F. J. Ackerman et al., "Synroc Production Using a Fluid-Bed Calciner," UCRL-87742 (September 1982)
67. G. E. Bingham and B. R. Wheeler, "Remote Design Criteria and Philosophy of the New Waste Calcining Facility," Proc. of 26th Conference on Remote Systems Technology, p 223 (1978)
68. R. R. Smith and G. E. Bingham, "The New Waste Calcining Facility Maintenance Features and Capabilities," Proc. of 26th Conf. on Remote Systems Technology, 230 (1978)
69. R. T. Jacobs, J. A. Carter, and A. C. Hohback, "Remote Processing Connectors for the New Waste Calcining Facility," Proc. of 26th Conf. on Remote Systems Technology, 241 (1978)
70. K. W. May and H. H. Loo, "A Remotely Replaceable and Testable Off-Gas Filter System for the New Waste Calcining Facility," Proc. of 26th Conf. on Remote Technology Systems, 250 (1978)
71. R. D. Fletcher, J. A. Carter, and K. W. May, "Remotely Replaceable Fuel and Feed Nozzles for the New Waste Calcining Facility Calciner Vessel," Proc. of 26th Conf. on Remote Systems Technology, 255 (1978)
72. M. E. Jacobson and H. H. Loo, "An Integrated Remote Process Sampling System for the New Waste Calcining Facility," Proc. of 26th Conf. on Remote Systems Technology, 260 (1978)

73. C. M. Cole and R. R. Smith , "The New Waste Calcining Facility/Idaho Chemical Processing Plant Remote Decontamination Facility," Proc. of 26th Conf. on Remote Systems Technology, 269 (1978)
74. W. Aschoff and R. Widmer, Industrial Metals Technology, Inc., Div. of National Forge, private communication
75. H. Larker, P. Hedvall, H. Hanes, D. Marzka, and J. Troops, ASEA Pressure Systems, Inc., private communication
76. P. E. Price, "Hot Isostatic Pressing in the Aerospace Industries," Metal Progress (February 1982)
77. R. Widmer, "Densification of Castings by Hot Isostatic Pressing," presented at the 26th Investment Casting Institute meeting, Phoenix, Arizona (October 1978)
78. C. W. Smith and F. X. Zimmerman, "HIP Equipment for Industrial Applications" and "The Design of Yoke Frame Multiple Ring Pressure Vessel," Autoclave Engineers, Inc., Erie, Pennsylvania (March 1979)
79. L. F. Grantham and J. F. Flintoff, "Spray Calcination of SRP Waste Composition for Ceramic Waste Forms," Proc. of the Amer. Nuc. Soc. Topical Meeting on the Treatment and Handling of Radioactive Waste, 445, Battelle Press (April 1982)
80. R. B. Rozsa and J. H. Campbell, "Disposal Casts for SRP High-Level Wastes in Borosilicate Glass and Crystalline Ceramic Waste Forms," UCRL-53315 (August 1982)

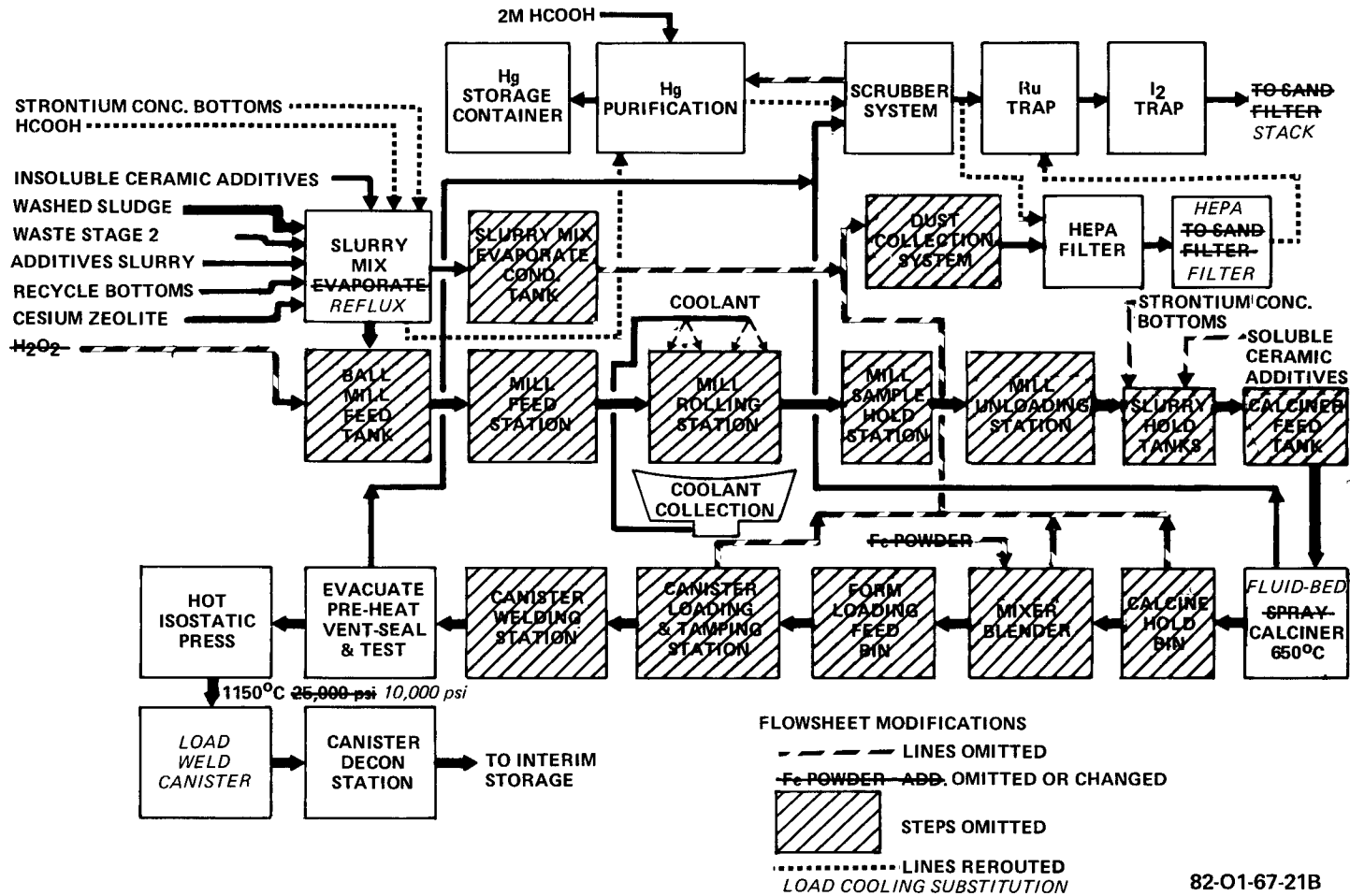
APPENDIX A

COMPARISON OF COSTS FOR MANAGEMENT OF SAVANNAH RIVER PLANT WASTE WITH COSTS DERIVED BY McDONNEL⁽⁵⁷⁾

Savannah River has performed a comparative economic evaluation using the glass and ceramic options to manage SRP wastes using the preliminary ceramics flowsheet derived 3 months after the start of the Ceramics Waste Alternative Development program. Since little ceramic engineering had been performed, this preliminary flowsheet was not optimized for ceramics and was largely developed from a knowledge of waste management techniques used in early glass processes. In the last 3 years since this preliminary process flow diagram was submitted, a number of processing improvements have been made. Due to the press of time, Savannah River was unable to incorporate these process developments in their economic evaluation.^(57,58) As will be shown below, using the modified ceramic flowsheet reduces costs considerably, primarily by reducing the ceramic immobilization capital and operating actual and contingency costs.

The preliminary ceramic process flowsheet⁽⁵⁸⁾ and plant layout used by DuPont⁽⁵⁸⁾ and Savannah River Laboratory⁽⁵⁷⁾ to evaluate the capital and operating costs are given in Figures A-1 and A-2. The processing lines, additives, and steps omitted in the revised flowsheet are shown cross-hatched in Figures A-1 and A-2. Rerouted lines and steps added in the revised flowsheet are dashed. Essentially one-half of the processing steps have been omitted in the revised version. Since operability of the ceramic process based on the preliminary flowsheet was judged to be twice as complex as the glass process by SRL, the operability of the ceramic process based on the revised flowsheet should be essentially equivalent to the glass process since half of the steps in the preliminary flowsheet have been omitted.

Similarly, the process layout based on the preliminary flowsheet has been cross-hatched to show the components (and the attendant processing area) omitted using the revised flowsheet. The ceramic processing canyon based on the preliminary flowsheet was $103 \text{ m} \times 20.7 \text{ m} = 3125 \text{ m}^2$ ($338 \text{ ft} \times 68 \text{ ft} = 22,984 \text{ ft}^2$)

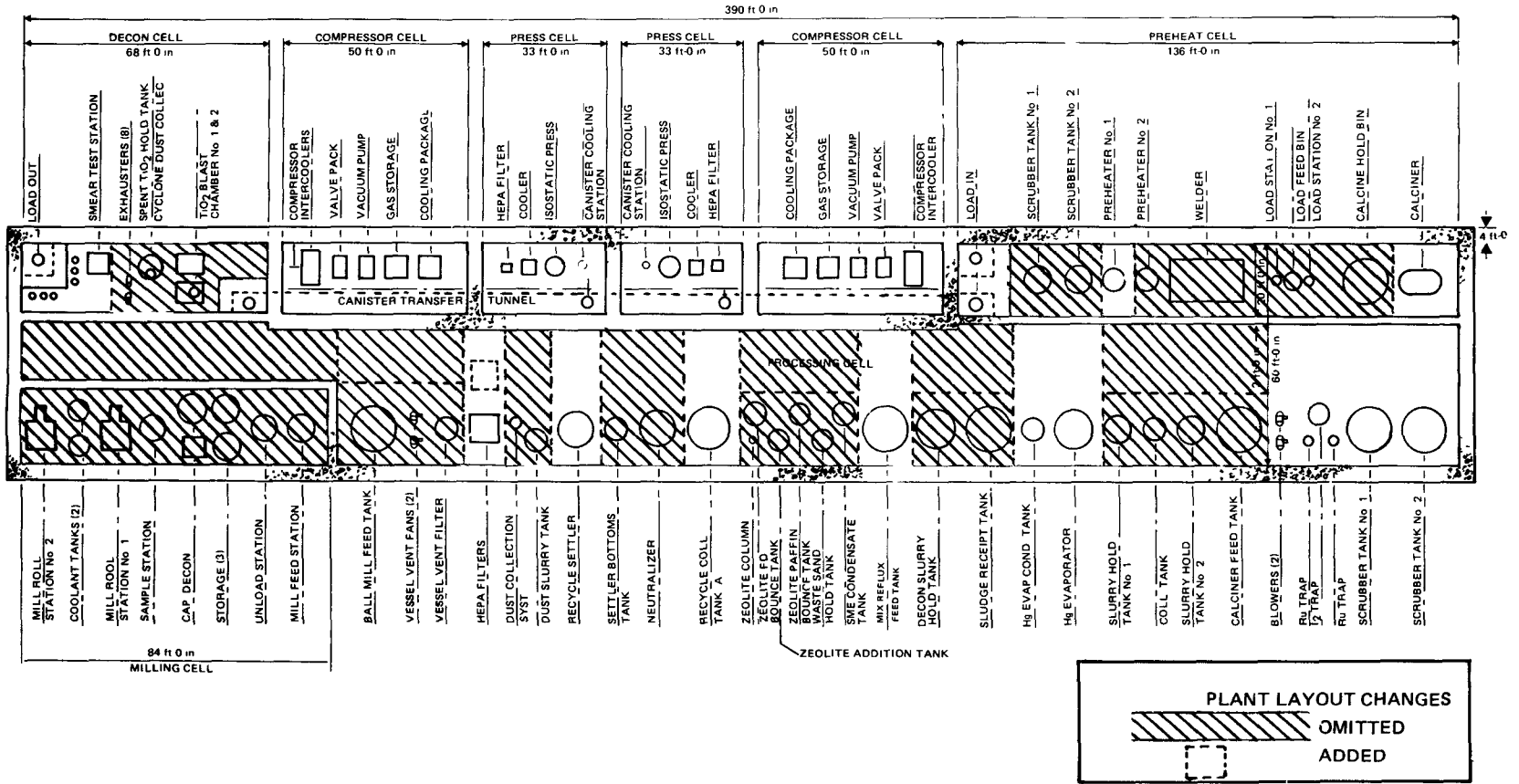


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Figure A-1. Modifications Made in the Preliminary Ceramic Process Flowsheet for Defense Waste

DOE/ET/41900-16
 (ESG-DOE-13397)

69



82-01-78-70A

Figure A-2. Modifications Made in the Preliminary Crystalline Ceramic Process Cell Arrangement

including the radiation walls around the canyon. Eliminating the cross-hatched area from the canyon changed the area to $39.9 \text{ m} \times 13.4 \text{ m} = 535 \text{ m}^2$ plus $71.3 \text{ m} \times 7.3 \text{ m} = 522 \text{ m}^2$ ($131 \text{ ft} \times 44 \text{ ft} = 5764 \text{ ft}^2$ plus $234 \text{ ft} \times 24 \text{ ft} = 5616 \text{ ft}^2$) for a total of 1057 m^2 ($11,380 \text{ ft}^2$) without rearranging the equipment. This is less than the SRL 1092- m^2 ($11,764\text{-ft}^2$) layout of the glass processing plant. By consolidating and rearranging the ceramic equipment to enhance operability, and by using off-gas processing techniques described in this report, the layout area can be reduced even further to 876 m^2 ($9,424 \text{ ft}^2$) as shown in the text.

The comparison of waste management costs using the SRL glass and ceramic flowsheets and the glass and ceramic flowsheets described herein is given in Table A-1. The waste management costs developed by SRL and in this report using the glass option are essentially identical, but there is a large difference in waste management costs using the ceramic option. The difference in ceramic costs reflects not only the difference in plant design but also the great amount of ceramic process development made in the last 3 years since the preliminary ceramic flowsheet was developed for Savannah River. Using the new flowsheet, the ceramic option SRP waste management costs have been estimated to decrease by \$1.3 billion from the costs derived by SRL.⁽⁵⁷⁾ This decrease is largely due to reduction of the canyon size as well as reduction of capital and operating contingencies due to ceramic process simplification and full-scale demonstration of processing equipment; minor decreases in costs were also made in development, canister, and a major decrease in repository allocations was made. The net result is that the ceramic option instead of being more costly by \$0.4 billion appears to be less costly than glass by \sim \$0.9 billion. A large reduction cost in ceramic waste management for SRP waste was also found in LLNL's economic evaluation⁽⁸⁰⁾ in which the ceramic costs were decreased about \$0.8 billion from the SRP estimate of \$2.9 billion to \sim \$2.1 billion. LLNL made this reduction by making minor revisions in the flowsheet, using the same contingencies for glass and ceramic for similar portions of the process, and by using tuff repository costs. Using the same methodology for the glass process, LLNL reduced the SRP waste management costs to \$2.1 billion using the glass option.⁽⁸⁰⁾

TABLE A-1
 COMPARATIVE COSTS USING GLASS AND CERAMIC WASTE FORMS TO MANAGE SRP WASTE
 (Millions of Dollars)

Item	SRP ⁽⁵⁷⁾		Rockwell (This Report)	
	Glass ^a	Ceramic ^b	Glass ^a	Ceramic ^{b,c}
Development	65	180	65	80
Tank farm	9	-	9	-
DWPF Stage 1 capital and support	650	1,100	569	571
DWPF operating	535	870	664	522
Canister procurement	103	131	57	49
Interim storage	78	30	78	30
Offsite transport	124	41	124	41
Repository	<u>945</u>	<u>528</u>	<u>945</u>	<u>312</u>
Total	2,509	2,880	2,511	1,605

^a10,300 canisters of glassified waste, 24-in.-diameter canisters

^b3,400 canisters of ceramic waste, 24-in.-diameter canisters

^cUsing revised flowsheet with well-developed technology