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ALTERNATIVES FOR VITRIFICATION OF EXISTING COMMERCIAL HIGH-LEVEL WASTE BY SPRAY CALCINATION/IN-CAN MELTING

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INTRODUCTION

Three vitrification flowsheet options have been investigated for immobilization of existing commercial high-level waste stored at the Western New York Service Center (WNYSC), West Valley, New York. The options were developed from process alternatives being considered for removal and solidification of radionuclides in the stored neutralized Purex waste and the acidic Thorex waste.(1,2) Laboratory glass development studies and process feasibility studies using the Spray Calciner/In-Can Melter process were explored. Initial results obtained from the laboratory investigations and the pilot plant testing using nonradioactive chemicals are reported.

The Spray Calciner/In-Can Melting (SC/ICM) Process(3) converts high-level waste into a borosilicate glass for long-term storage of the radioactive material. This process is a candidate process for immobilization of this commercial waste; however to date the specific waste form and process for waste immobilization has not been chosen. The SC/ICM process was developed at the Pacific Northwest Laboratory (PNL), operated by the Battelle Memorial Institute for the Department of Energy.

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BACKGROUND

Two types of high-level waste generated from the chemical reprocessing of spent nuclear reactor fuel are stored at the WNYSC. The largest waste volume was generated from reprocessing 624.5 metric tonne equivalent uranium fuel using the Purex flowsheet. The acidic Purex process waste was neutralized with sodium hydroxide before being transferred to Tank 8D2, a carbon steel storage tank. Waste neutralization resulted in precipitation of most metals and fission products except alkali metal nitrates and hydroxides such as sodium and cesium into a sludge layer on the tank bottom. The total neutralized waste volume is approximately 600,000 gal (2.27×10^6 ℓ) of which approximately 570,000 gal (2.15×10^6 ℓ) is supernate and about 30,000 gal (1.13×10^5 ℓ) is sludge.

The second waste type was generated from the reprocessing of 16 metric tonne uranium enriched thorium fuel. The total acidic waste volume estimated to be 12,000 gal (4.5×10^4 ℓ) is stored in Tank 8D4, a stainless steel storage tank. Major chemical components of each type of waste are summarized in Table I.

FLOWSHEET OPTIONS FOR WASTE VITRIFICATION

Three flowsheet options have been investigated for vitrification of the existing high-level waste stored at the WNYSC. The differences in options result from pre-treatment of the waste prior to vitrification and various ways of combining the waste fractions (Tank 8D2 sludge, Tank 8D2 supernate, and Tank 8D4 contents). All three waste fractions can be converted to a high-level waste form. However, in terms of volume reduction of the final high-level waste form, it is necessary to vitrify only the radioactive portions of the waste.

Vitrification of the high-level waste stored at the WNYSC can be achieved by anyone of the following options:

- Vitrification of Tank 8D2 sludge combined with fission products recovered from the Tank 8D2 supernate and the acidic Thorex waste in Tank 8D4 (Option 1).
- Vitrification of the Tank 8D2 sludge with fission products recovered from the Tank 8D2 supernate separately from the vitrification of Tank 8D4 waste (Option 2).

- Vitrification of the combined contents of Tank 8D2 and Tank 8D4 (Option 3).

TABLE I. Chemical Composition of Neutralized High-Level Waste Stored in Tank 8D2 and Acidic Waste Stored in Tank 8D4[(a)] (mole/liter)

Component	Neutral Waste, Tank 8D2 Supernate	Neutral Waste, Tank 8D2 Sludge[(b)]	Acidic Waste Tank 8D4
Al	0.01	0.09 (1.8)	0.35
Cr, Ni	N.A.	0.04 (0.08)	N.A.
Fe	N.A.	0.29 (5.8)	N.A.
Na, K	6.78	N.A.	N.A.
Th	N.A.	N.A.	1.46
Cl	0.01	N.A.	0
F	0.01	N.A.	0.1
P	0.08	N.A.	0.04
SO_4	0.28	N.A.	N.A.
HNO_3	N.A.	N.A.	1.03
Curies, Total (1973)	4.0×10^7	2.7×10^8	2.5×10^6
Volume, gallon	570,000	30,000	12,000
Self-heating valve (Btu/h/gal)	0.7	(140)	3

(a) Reference - TID-28905-2.
(b) Numbers in parenthesis are based on wet sludge volume.
N.A. Not applicable.

A process flowsheet showing the major steps for the immobilization of stored high-level waste by Option 1 is summarized in Fig. 1. The basic processing steps involve separation of the Tank 8D2 neutral waste into a supernate and sludge fraction. The supernate is passed through ion exchange columns to remove strontium, cesium and plutonium. Recovered fission products along with the sludge are blended with the acidic waste stored in Tank 8D4. The decontaminated supernate is converted to a salt cake for storage.

The flowsheet for Option 2 is diagrammed in Fig. 2. This flowsheet is essentially identical to Option 1 except for the separate vitrification of the acidic Thorex waste and neutral waste. The flowsheet for treatment of the neutral waste is similar to that being considered by the Savannah River Plant for immobilization of high-level waste stored at the plant site.(4) Separate vitrification of the Thorex waste would demonstrate solidification of high-level waste resulting from the thorium fuel cycle.

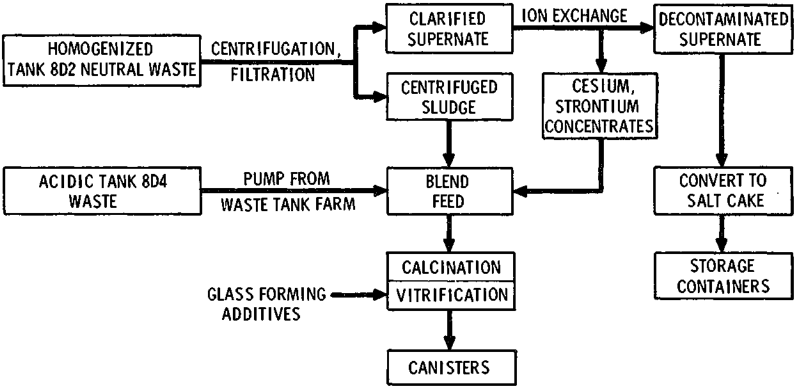

FIGURE 1. Vitrification of Combined Tank 8D2 Sludge Fission Products Recovered from Tank 8D2 Supernate and Tank 8D4 Acid Thorex Waste

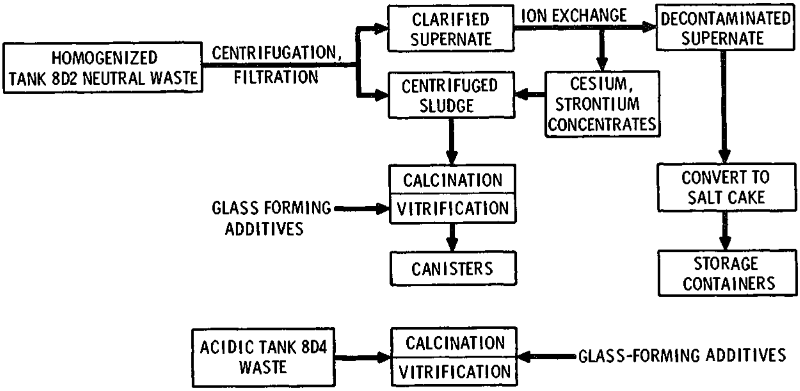

FIGURE 2. Vitrification of Tank 8D2 Neutral Sludge With Recovered Fission Products and Tank 8D4 Acid Thorex Waste

Option 3 is depicted in Fig. 3. This alternative considers the vitrification of a blended mixture of Tank 8D2 neutral waste with Tank 8D4 acidic Thorex waste. The Tank 8D2 supernate and sludge would be slurried together before blending with the acidic Thorex waste.

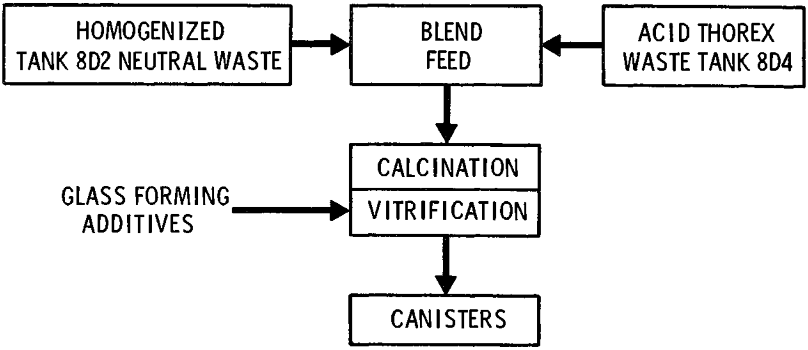

FIGURE 3. Vitrification of Combined Tank 8D2 Sludge and Supernate and Tank 8D4 Acid Thorex Waste

Simulated waste compositions as calcined oxides for each of the three options identified are summarized in Table II. These waste compositions were based on anticipated average compositions which can vary as a result of waste processing operations and chemical variations within the two storage tanks.

GLASS DEVELOPMENT

Borosilicate glass is the waste form which has been most commonly investigated using the PNL Spray Calciner/In-Can Melter Process. Calcined waste is combined with glass-forming chemicals in the in-can melter. This mixture is melted to form a stable vitreous waste form. The glass composition developed for a particular waste composition reflects a compromise between conflicting requirements; for example, the glass must have low enough viscosity for processing, yet possess adequate chemical durability to satisfy radionuclide immobilization criteria.

TABLE II. Chemical Compositions of Simulated Wastes for Different Flowsheet Options (Oxide Form, wt%)

Component (Oxide Form)	Tank 8D2 Sludge, Fission Products, Tank 8D4 (Option 1)	Tank 8D4 Thorex Waste (Option 2)	Tank 8D2 Plus Tank 8D4 (Option 3)
Al_2O_3	1.4	7.8	0.4
Na_2O	3.0	3.7	70.7
K_2O	--	1.6	--
ZrO_2 (a)	8.4	48.6	1.5
Cr_2O_3	3.5	7.0	0.9
Fe_2O_3	55.5	27.6	10.3
NiO	1.6	3.6	0.4
F	0.1	--	0.2
P_2O_5	14.5	--	2.7
B_2O_3	0.3	--	--
MnO_2	2.2	--	0.4
MoO_3	1.2	--	0.3
Nd_2O_3 (b)	3.5	--	0.6
SO_4	0.3	--	11.0
Rare Earth (c) Mixture	4.7	--	0.7
	100	100	100

(a) ZrO_2 chemical substitute for ThO_2, molar basis.

(b) Nd_2O_3 chemical substitute for U_3O_8, molar basis.

(c) Fission products simulated using a commercial rare earth mixture containing (wt%, 0.2 Y_2O_3, 24.0 La_2O_3, 48.0 CeO_2, 5.0 Pr_6O_{11}, 17.0 Nd_2O_3, 3.0 Sm_2O_3, 0.8 Eu_2O_3, 2.0 Gd_2O_3).

Initial laboratory glass formulations developed for process testing of the vitrification options have the compositions shown in Table III. Simulated waste chemicals were combined with glass-forming chemicals in batches of 100 g. Melt temperatures were 1050°C. The glasses developed do not necessarily represent the final glass form. Optimization of the glass formulation requires feedback from the laboratory glass characterization and the engineering-scale glass produced from the process. Several iterations may be necessary to define the final glass former composition.

The glass developed for Option 1 reflects the high iron content present in the waste. Iron by itself causes no processing problems; however, if high quantities of alumina (>10-15% in the calcined waste) are present in the waste because of compositional variations, severe precipitation of a nickel-ferrite spinel from the glass would probably occur. It is felt that fission products can collect at the grain boundaries, thereby becoming more leachable from the glass.

The glass developed for the Thorex waste (Option 2) has a low silica content compared to the other glasses. This is due to the high alumina level in the waste. Both silica and alumina act to increase the glass viscosity. Good chemical durability of the glass will be achieved due to the high levels of titanium dioxide and zirconium dioxide. The laboratory glass developed has relatively low viscosity and should be easily processable. The glass for immobilization of the sludge and recovered fission product waste will be identical to the glass developed for Option 1. The high neutral waste volume dominates the much smaller Thorex waste volume when the two wastes are blended.

A primary concern in developing a vitreous form to immobilize the waste from Option 3 is the high sodium content of the composite waste. The high sodium oxide content of the calcined waste (Table II) restricts the waste loading in the glass to about 20 wt%. Sodium oxide degrades the chemical durability of the glass. However, it enhances the melting behavior by lowering the glass viscosity. The high sodium oxide content of the calcined waste necessitates that the glass former be added as batch chemicals which melt more readily than a premelted frit in the process.

Laboratory studies have shown that sodium sulphate present in the calcined waste can lead to the formation of a water soluble phase which separates from the glass product.(6) Fission products,

TABLE III. Glass Former Chemical Mixture for Flowsheet Options

Component	Tank 8D2 Sludge, Fission Product, Tank 8D4 (Option 1)	Tank 8D4 Thorex Waste (Option 2)	Tank 8D2 plus Tank 8D4 (Option 3)[a]
SiO_2	49.3	37.0	63.7
B_2O_3	16.4	17.0	12.5
Li_2O	2.7	2.9	1.4
Na_2O	15.1	16.0	--
K_2O	1.4	5.7	--
CaO	2.7	10.0	2.6
TiO_2	2.7	5.7	10.4
ZnO	--	5.7	--
MgO	2.7	--	2.6
BaO	2.7	--	1.4
ZrO_2	2.7	--	5.5
	100	100	100
Glass Former to Waste Loading	70:30	73:27	72:28
Metric Tonne Glass Produced From Flowsheet	550	126	2200

(a) This glass contains 7.8×10^{-2} gram carbon/gram waste as a reducing agent.

principally cesium and rubidium, would tend to concentrate in this water soluble sodium sulphate phase. The sulphate ion can be reduced to SO_3 using silicon metal or graphite. Reduction of the sulphate ion to sulfur trioxide gas which leaves the system eliminates sodium sulphate phase separation. Laboratory studies indicate that sulfur has a limited solubility in glass as sulfur trioxide (solubility ∿0.5 wt%).(7)

SPRAY CALCINER/IN-CAN MELTER PROCESS DESCRIPTION

The SC/ICM process has been developed extensively for solidification of high-level waste as a borosilicate glass. The SC/ICM system is shown schematically in Fig. 4. A picture of the nonradioactive pilot scale SC/ICM used for this study is shown in Fig. 5.

In the SC/ICM process, high-level liquid waste is atomized by air by a commercially available spray nozzle into droplets of approximately 70 μ size. These droplets are dried and generally decomposed to metal oxides as they fall through the electrically-heated spray calciner furnace. The temperature of the spray calciner furnace varies from 300 to 800°C depending upon the high-level waste characteristics. The calcine powder formed is stoichiometrically mixed with glass-forming chemicals as it falls from the spray calciner into the receiving canister. The calcine/glass former chemical mixture is heated and melted inside the receiving canister to form a borosilicate glass. The nominal temperature of operation of the in-can melter furnace is 1050°C. Glass production rates using the pilot-scale spray calciner in-can melter system vary between 10 and 50 kg/h depending upon the diameter of canister being used.

Offgases from the SC/ICM process consist primarily of water vapor, NO_x from nitrate decomposition, and possibly volatile forms of sulfur, chloride and fluoride. Volatile radionuclides could include ruthenium and iodine along with trace amounts of cesium, technetium, antimony and tellurium. Mercury, if present in the high-level waste, will also be volatile from the process. These components are easily removed by treatment of the offgas stream.

NONRADIOACTIVE PILOT PLANT EXPERIENCE

A pilot-scale SC/ICM system has been used to evaluate process feasibility of the waste vitrification options. Four canisters of waste glass have been produced using nonradioactive chemicals. The canisters are 8 inches in diameter having a glass fill height of 36 inches. Eighty to ninety kilograms of vitreous product is produced during a typical test.

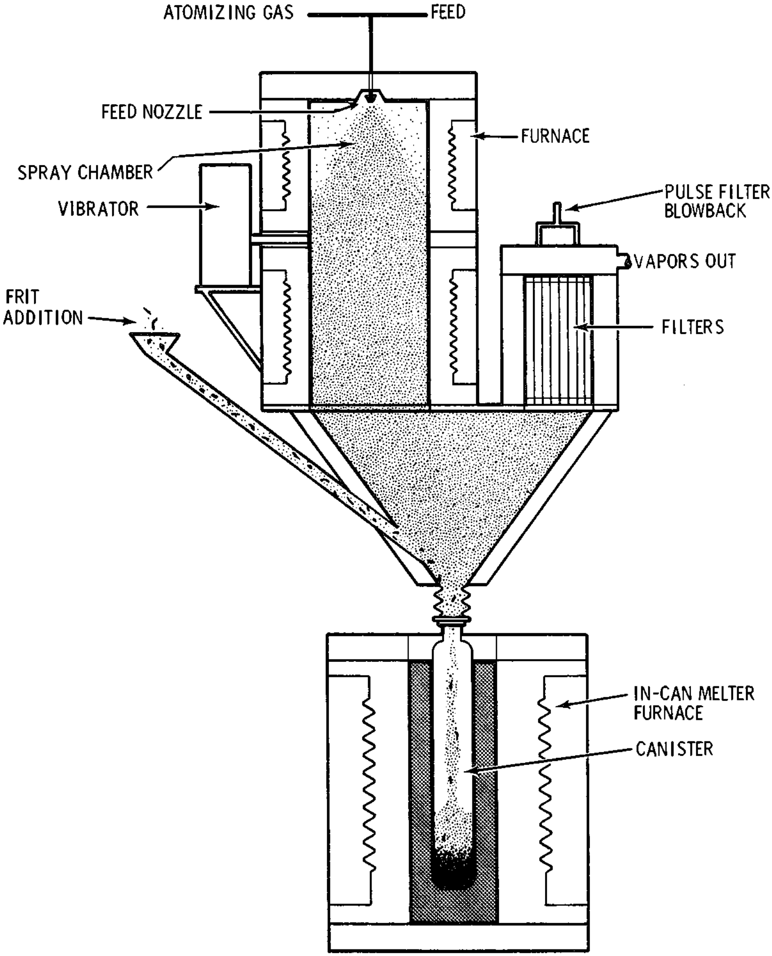

FIGURE 4. Schematic Spray Calciner/ In-Can Melter Process

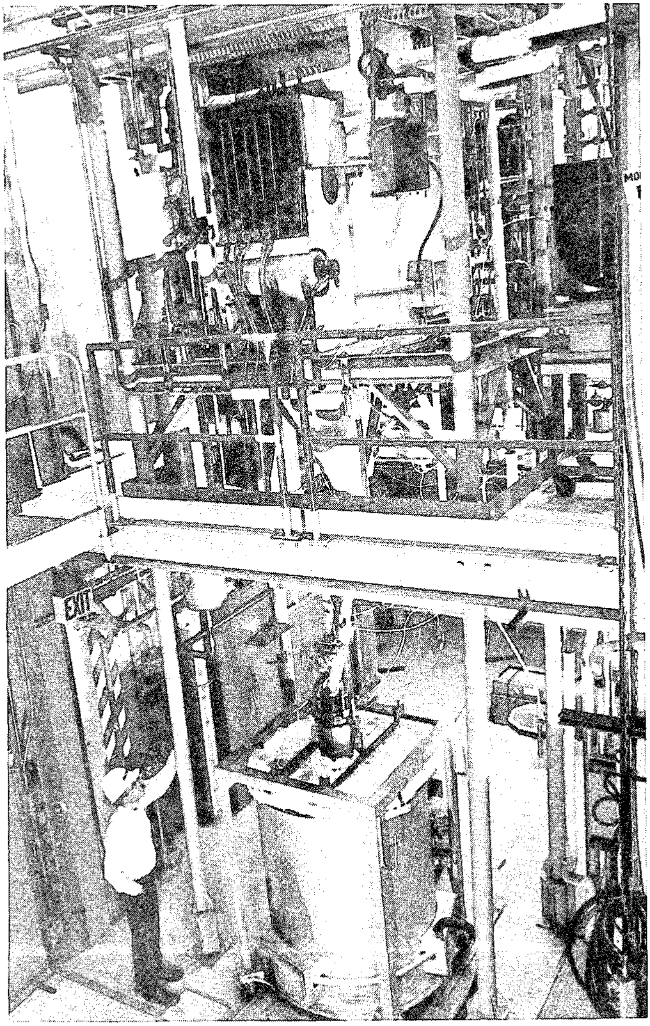

FIGURE 5. Nonradioactive Pilot-Scale Spray Calciner/In-Can Melter Process

The four canisters of glass produced represent flowsheet Option 1 (one canister), flowsheet Option 2 (one canister of neutral waste glass) and flowsheet Option 3 (two canisters). The production of a glass canister from flowsheet Option 3 required the use of a reducing agent. Silicon metal was added to the glass former mixture for one canister, and graphite was added to the glass former mixture for the other canister. The purpose of the reducing agent additive was to volatilize the sulphate in the waste and improve the product properties.

Flowsheet Option 3, Vitrification of Tank 8D2 Contents Plus Tank 8D4 Simulated Waste

The waste composition resulting from the blending of Tank 8D2 contents and Tank 8D4 contents (Option 3) has high concentrations of sodium, nitrate, nitrite and sulphate. The supernate composition dominates the waste characteristics due to its large relative volume and high chemical content. The sodium concentration in the actual waste formed from blending Tank 8D2 and Tank 8D4 would be approximately 6.5 molar. The waste composition was diluted in experimental tests to lower the solids loading in the spray calcine feed making the waste processable in the experimental system. This lowered the sodium concentration from 6.5 to 4.0 molar. The ratio of sodium to all other cations in this waste is approximately twenty to one. Calcine resulting from this feed mixture melts in the temperature range 350 to 400°C primarily because of the high sodium concentration. The calciner was operated at a temperature of 350 to 400°C to prevent sintering of calcine on the calciner walls. This operating method results in incomplete calcination of the waste feed materials.

Inspection of the calciner barrel after both tests showed no visible buildup of sintered calcine. The feed processing rate in each test was 30 ℓ/h, producing a glass product at a rate of 10 kg/h. The run was completed without any process or equipment problems.

Silicon metal and graphite were used as reducing agents to volatilize sulphate in the production of the first and second canisters, respectively. The reducing agents were added on a three to one molar basis with the sulphate ion. The weight percent sulphate removal was ∿89% with silicon metal as a reducing agent and ∿30% with graphite as a reducing agent. Visual inspection of the canister wall revealed extensive corrosion when silicon metal was added as the reducing agent. This corrosion can be controlled by reducing the silicon metal addition rate. Sodium sulphate phase separation was not noticeable in either canister of glass produced.

Leach test results reported as weight percent lost and volume percentage crystallinity of the glass in which silicon was used as the reducing agent is summarized in Table IV. The standard Soxhlet leach test was conducted over a 24-hour period in 100°C deionized water. The pH4 leach test was conducted using a sodium acetate buffered acetic acid solution at room temperature for 19 hours. The difference in results between the laboratory and pilot-plant data reflects primarily the difference in waste calcine loading in the glass. The presence of crystals in the glass indicate the formation of one or more separate crystalline phases which have not been identified. Selected physical properties of the glass are also summarized in Table IV.

TABLE IV. Physical Characteristics of Laboratory and Pilot-Plant Glasses - Tank 8D2 Plus Tank 8D4 Waste - Silicon Metal Added as Reducing Agent

Leach Test Results (wt% lost)

	Soxhlet	pH4
Laboratory Glass	8.0	0.5
Pilot-Plant Glass	3.3	2.26

Physical Properties

Crystallinity	7%
Specific Heat (cal/gram)	.18 to .22 (100-450°C)
Thermal Expansion	1.12×10^{-5} in./°C (100-400°C)
Softening Point Temperature	535°C

The glass former mixture for flowsheet Option 3 does not contain any alkali material (Na_2O, K_2O). As a result, the glass formers do not melt at in-can melter processing temperatures of 1020 to 1050°C. The sodium oxide in the calcined waste is a necessary component to make a durable and processable glass. The relatively good leach results of the pilot-plant glass reflect the ability of the waste calcine to become soluble in the glass former mixture.

Flowsheet Option 1, Vitrification of Tank 8D2 Sludge, Recovered Fission Products and Tank 8D4 Simulated Waste

A third canister of nonradioactive waste glass was produced using the flowsheet for Option 1. The waste composition resulting from this flowsheet has a high solids content. The simulated waste was diluted a factor of 15 from the flowsheet to make the liquid waste pumpable in the pilot-plant feed system. The spray calciner feedrate for the test averaged 27 ℓ/hour, corresponding to a glass production rate of 10 kg/hour. Glass formers were added as premelted but with a size range of -20 to +80 mesh.

The glass produced in the pilot plant has leach rates which are greater than the laboratory glass. The reason for this is the higher than expected waste loading in the glass. Spinel was not present in the glass. The glass product was homogeneous with no separate phases identified.

Calciner operating temperatures for this experiment were 700 to 750°C. This higher temperature of operation increases the spray calciner feed capacity. The higher operating temperature of the calciner can be achieved because of the higher melting point of the calcine (∿1000°C).

Leach test results and selected physical properties are summarized in Table V.

TABLE V. Physical Characteristics of Laboratory and Pilot-Plant Glasses - Tank 8D2 Neutral Sludge Plus Tank 8D4 Thorex Waste

Leach Test Results (wt% lost)

	Soxhlet	pH4
Laboratory Glass	2.5	0.5
Pilot-Plant Glass	9.1	20.1

Physical Properties

Crystallinity	No spinel present
Specific Heat (cal/gram)	.18 to .25 (100 to 450°C)
Thermal Expansion	9.93×10^{-6} in./°C (100 to 400°C)
Softening Point Temperature	525°C

Flowsheet Option 2 - Vitrification of Tank 8D2 Neutral Sludge and Recovered Fission Products

A fourth canister of nonradioactive waste glass was produced using a simulated waste representative of the neutral waste resulting from flowsheet Option 2. The glass composition for this waste is very similar to the glass as product from flowsheet Option 1.

Leach test results for the pilot-plant glass produced are summarized in Table VI. These leach test results are compared to the borosilicate glass, 76-68. This reference glass, 76-68, demonstrates good physical and chemical properties. Leach test results for all pilot-plant glasses produced are comparable to the referenced glass. The leach rate of the pilot-plant glasses can be improved with the appropriate glass former modifications.

TABLE VI. Leach Test Comparison - Tank 8D2 Neutral Sludge and Recovered Fission Products with Borosilicate Glass 76-68

Leach Test Results (wt% lost)	Soxhlet	pH4
Pilot-Plant Glass	5.8	1.2
76-68	1.6	0.1

CONCLUSIONS

This study has shown that the Spray Calciner/In-Can Melter process can produce a high quality glass product from the three flowsheet options considered for the immobilization of the high-level waste stored at West Valley, New York. The glass products produced from the three flowsheet options compare with the chemical durability of a well-developed reference borosilicate glass. Additional waste formulations and process development studies can improve product quality.

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