2

WSRC-RP-93-01111-Rev.1

OAK RIDGE NATIONAL LABORATORY WEST END TREATMENT FACILITY SIMULATED SLUDGE VITRIFICATION DEMONSTRATION (U)

by

C. A. Cicero

Westinghouse Savannah River Company
Savannah River Site
Aiken, South Carolina 29808

D. F. Bickford
D. M. Bennert
T. J. Ocercamp

DOE Contract No. DE-AC09-89SR18035

WSRC-RP-93-1111
Revision ~~0~~ 1

CLEMSON UNIVERSITY
DEPARTMENT OF ENVIRONMENTAL SYSTEMS ENGINEERING
TECHNICAL TASK PLAN

OAK RIDGE NATIONAL LABORATORY WEST END TREATMENT FACILITY SIMULATED SLUDGE VITRIFICATION DEMONSTRATION (U)

C.A. Cicero and D.F. Bickford
Westinghouse Savannah River Co.

D.M. Bennert and T.J. Overcamp
Clemson University

Clemson University .
Department of Environmental
Systems Engineering
Anderson, SC 29625

Westinghouse Savannah River Co.
Savannah River Technology Center
Aiken, SC 29808

DISCLAIMER

WSRC-RP-93-1111
Revision 1

Keywords: Glass, ORNL Vitrification, sludge, RCRA, LDR, low level mixed waste

CLEMSON UNIVERSITY DEPARTMENT OF ENVIRONMENTAL SYSTEMS ENGINEERING TECHNICAL TASK PLAN

OAK RIDGE NATIONAL LABORATORY WEST END TREATMENT FACILITY SIMULATED SLUDGE VITRIFICATION DEMONSTRATION (U)

C.A. Cicero and D.F. Bickford
Westinghouse Savannah River Co.

D.M. Bennert and T.J. Overcamp
Clemson University

Publication Date: 1/26/94

Clemson University
Department of Environmental
Systems Engineering
Anderson, SC 29625

Westinghouse Savannah River Co.
Savannah River Technology Center
Aiken, SC 29808

APPROVALS

Westinghouse Savannah River Company

M. J. Plodinec
Manager, Glass Technology Group
Savannah River Technology Center

D. F. Bickford
Technical Representative, Glass Technology Group
Savannah River Technology Center

K. E. Mottel
Quality Assurance Representative, Glass Technology Group
Savannah River Technology Center

Department of Environmental Systems Engineering

T.J. Overcamp
Principal Investigator, Clemson University
Department of Environmental Systems Engineering

D.M. Bennert
Task Leader, Clemson University
Department of Environmental Systems Engineering

CONTENTS

CONTENTS

List of Acronyms

AA:	Atomic Absorption
BDAT:	Best Demonstrated Available Technology
CU:	Clemson University
DOE:	United States Department of Energy
EPA:	Environmental Protection Agency
GC:	Gas Chromatograph
GD:	Glow Discharge
GTG:	Glass Technology Group
IC:	Ion Chromatography
ICP:	Inductively Coupled Plasma
ISE:	Ion Selective Electrode
MWIP:	Mixed Waste Integrated Program
ORNL:	Oak Ridge National Laboratory
PCT:	Product Consistency Test
PNL:	Pacific Northwest Laboratory
RF:	Rocky Flats Plant
SEM:	Scanning Electron Microscopy/Microscope
SCDHEC:	South Carolina Department of Health and Environmental Control
SCUREF:	South Carolina Universities Research and Education Foundation
SRS:	Savannah River Site
SRTC:	Savannah River Technology Center
TCLP:	Toxicity Characteristic Leaching Procedure
XRD:	X-ray Diffraction
XRF:	X-ray Fluorescence
WETF:	West End Treatment Facility
WSRC:	Westinghouse Savannah River Company
WTF:	West Tank Farm

OAK RIDGE NATIONAL LABORATORY WEST END TREATMENT FACILTIY SIMULATED SLUDGE VITRIFICATION DEMONSTRATION

C.A. Cicero and D.F. Bickford
Westinghouse Savannah River Co.
Savannah River Technology Center
Aiken, SC 29808

D.M. Bennert and T.J. Overcamp
Clemson University
Department of Environmental Systems Engineering
Anderson, SC 29625

INTRODUCTION

TASK DISCUSSION

Technologies are being developed by the US Department of Energy's (DOE) Nuclear Facility sites to convert hazardous and mixed wastes to a form suitable for permanent disposal. The preferred disposal method would be one that is capable of consistently producing a durable, leach resistant wasteform, while simultaneously minimizing disposal volumes. Vitrification, which has been declared the Best Demonstrated Available Technology (BDAT) for high-level radioactive waste disposal by the EPA[1], is capable of producing a highly durable wasteform that minimizes disposal volumes through organic destruction, moisture evaporation, and porosity reduction. However, this technology must be demonstrated over a range of waste characteristics, including compositions, chemistries, moistures, and physical characteristics to ensure that it is suitable for hazardous and mixed waste treatment.

The Department f Environmental Systems Engineering at Clemson University (CU) has been selected by the Westinghouse Savannah River Company (WSRC), under SCUREF Task Order #121, to demonstrate vitrification of simulated wastes that are considered representative of wastes found throughout the DOE complex. These wastes are typically wastewater treatment sludges that are categorized as listed wastes due to the process origin or organic solvent content, and usually contain only small amounts of hazardous constituents.

The Oak Ridge National Laboratory's (ORNL) West End Treatment Facility's (WETF) sludge is considered one of these representative wastes. The WETF is a liquid waste processing plant that generates sludge from biodenitrification and precipitation processes. The uniqueness of this sludge is that it is chiefly inorganic, but contains greater than 1% organics. Presently, the plant processes 20,000,000 liters of waste per year, and has a current inventory of approximately 250,000 ft^3.[2] An alternative wasteform is needed since the waste is currently stored in epoxy coated carbon steel tanks, which have a limited life. Since this waste has characteristics that make it suitable for vitrification with a high likelihood of success, it was identified as a suitable candidate by the Mixed Waste Integrated Program (MWIP) for testing at CU. The areas of special interest with this sludge are 1) minimum nitrates, 2) organic destruction, and 3) waste water treatment sludges containing little or no filter aid.

ORNL WETF WASTE DESCRIPTION

The WETF process consists of biodenitrification and heavy metal precipitation using hydrated lime. After waste processing, the sludge bottoms from the WETF clarifier are transferred to tank numbers F-7, F-8, F-9, and F-13 for storage. These tanks are located in the West Tank Farm (WTF), which is why the WETF sludges are also referred to as WTF sludges. Approximately 90% of the sludge consists of calcium carbonate and biomass generated from the biological destruction of nitrate ions. The balance is generated from the hydroxide precipitation of heavy metals in a lime treatment process.[2]

Uranium is the primary isotope of concern in the waste stream, but the sludge also contains isotopes of neptunium, technetium, and thorium. The uranium concentration averages about 1369 ppm, with ^{235}U contributing 0.42% of the total uranium. The sludge also contains chromium, nickel, lead, and a low concentration of organics. From a regulatory perspective, this means that the sludge contains solvents or components to make it a F001, F002, F005, or F006 RCRA waste.[2]

An analysis of ORNL WETF sludge from tank F-7 was performed by ORNL and the results based on a dry weight basis are provided in Table 1.[2] All constituents from the analyses are included, even if present in very small amounts. X-ray diffraction (XRD) of the dried sludge revealed that $CaCO_3$ (calcite) was the predominant crystalline phase.[2] The water weight loss of the sludge was 71.4 ± 0.8% and the pH was 8.9 ± 0.2.

The characteristics of the data for tank F-7 should be considered typical of tanks F-8, F-9, and F-13, since the sludge from F-7 appears fairly consistent in composition.[2] Recently completed chemical analysis and x-ray diffaction analyses of F-9 sludge verified this consistency.[3,4]

TABLE 1 - ORNL WETF WASTE COMPOSITION

Constituent	Concentration (µg/g)
Aluminum	50,300
Barium	540
Berylium	13
Cadmium	44
Calcium	267,000
Chloride	628
Chromium	410
Copper	998
Cyanide	3.3
Iron	14,300
Lead	240
Lithium	397
Magnesium	9,400
Nickel	1,100
Oil and Grease	12,700
Organic Carbon	592
Phenol	114
Phosphorous	3,000
Silicon	660
Silver	23
Sodium	21,200
Uranium	1,370
Zinc	250

Vitrification and subsequent delisting of WETF sludge is advantageous for the following reasons:

- Large volume reductions of the waste can be obtained.
- Glass has been determined to be the BDAT for high level radioactive liquid waste.[1]
- Glass has a very high potential for being delisted which would avoid the cost of having to use an expensive RCRA hazardous waste/mixed waste storage vault. Direct disposal to a shallow landfill could be utilized instead.
- Ni, U, and other hazardous metal releases from glass wasteforms during leach testing are low due to the chemical bonding of metal oxides in the glass structure; thus, Ni and U releases would not be much of a concern.[5]
- A higher tolerance exists to variations in waste composition with glass formulations.

- Stirred glass melters continuously stir the melt so that the glass is homogeneous at lower temperatures than achieved with conventional vitrification.[6] High-temperature melters permit a wider variation in glass composition, and can result in homogeneous and very durable glasses.

Laboratory scale research performed by R. N. Peters of Battelle, Pacific Northwest Laboratory (PNL) with a simulant of the ORNL WETF sludge was successful in producing twelve different glass compositions.[7] However, his surrogate did not contain aluminum, iron, magnesium, or sodium, which are present in the WETF sludge, see Table 1. To make up for the lack of these glass forming additives in his surrogate, with the exception of iron and magnesium, he used oxides of these elements as the glass making additives in addition to SiO_2, CaF_2, and B_2O_3. His glasses varied from a 17 to 48 wt% waste loading. Preliminary TCLP results have indicated that these glasses will pass the RCRA Land Disposal Requirements imposed by the EPA.[7]

FACILITY DESCRIPTION

WSRC and the Department of Environmental Systems Engineering at CU have established a 2000 square foot facility as a site dedicated to bench scale and pilot scale vitrification research. This laboratory is equipped with lab bench areas, hooded work areas, and supporting equipment. Melting equipment capable of pilot scale waste vitrification has been supplied by Stir-Melter, Inc., and EnVitCo, Inc. The melting research area consists of a closed building with sufficient power for melter and systems operation, the two melters, complete offgas treatment facilities including quenching, neutralizing, and filtration, and support equipment sufficient to operate the melters and conduct the necessary sampling and testing.

Melter Systems

The Stir-Melter, Inc., melter is a 1/4 square foot stirred tank melter, and is a lab-scale/pilot-scale of the 9 square foot surface area WV-9 melter currently being considered for use by WSRC. It is capable of producing about 250 pounds of glass per day from dry feed. The EnVitCo, Inc., melter is a portable pilot-scale vitrification unit, which is a rugged, refractory lined, cold-top melter using four horizontally mounted molybdenum electrodes. Both melters will be fitted with in-chamber gas manifold systems to accommodate feed of combustion fuels, and inert and oxidizing atmospheres. Combustion fuels and oxidizing atmospheres will be used to assist and control the oxidation of the organic fractions in the waste, and inert atmospheres will allow for tank drainage from hot state without oxidation of molybdenum electrodes.

The Stir-Melter vitrification strategy is unique due to the chamber design, electrode/heating concept, and its agitation method. The melter utilizes an Inconel® melt chamber, versus traditional refractory chambers. Inconel® is used because it serves as one of the two electrodes (the second is the Inconel® impeller), and less refractory contact decreases the amount of contaminated material generated during maintenance or dismantlement when the unit is used to process hazardous or mixed wastes. By decreasing the amount of contaminated material generated, significant cost savings can be achieved. The Inconel® impeller also provides a stirring action that results in much higher mixing and production rates than can be achieved by convective mixing alone for melter of this size. The impeller height can be adjusted to create a two-phase solution in the chamber; one phase consisting of dense molten glass, the second phase entrained with air and other gases from the melt. The gas loaded glass has much lower viscosities, and can be mixed very rapidly, which improves the rate at which solids can be melted into the glass.

The EnVitCo melter is designed to reduce the volatile losses of hazardous compounds. This is achieved by maintaining a layer of low temperature glass and waste (about 200°C) on the top of the high temperature molten glass (1260-1370°C). As materials move down into higher temperature zones of the melt, the volatile fractions rise and are condensed and trapped in the upper batch. Wastes that have high metal content and high solids fractions may be suitable to the cold top melter vitrification process due to high operating temperatures, lower turbulence, and no moving parts to damage. The cold top melter is theoretically capable of much greater waste volume reductions due to the higher vitrification temperatures. The temperature of the cold top melter can be adjusted to minimize volatility, or to maximize throughput or durability.

MELTER FEED

Waste Sludge Simulant

The analyzed WETF composition given in Table 1 was used to develop a surrogate waste formulation. Cyanide, beryllium, lithium, silicon, silver, and zinc were not included in the surrogate composition due to the small quantities present and since they are not RCRA metals of concern. In addition, cyanide is destroyed by the high operating temperatures of vitrification and the behaviour of lithium has been characterized in the high level waste programs, so their effects on glass vitrification do not have to be studied. Molybdenum was used as a substitute for uranium, since it is not radioactive. As stated earlier, tests have shown that uranium releases during leaching are low due to the chemical bonding of the glass structure,[5] so the omission of uranium will not greatly affect the final glass product. The composition in Table 2 includes contributions from dried yeast, while dodecane is used for the oil and grease surrogate. Dried yeast was used as the biomass surrogate because of its availability, the lack of FDA restrictions, and since its gross chemical composition is similar to bacteria. Dodecane was used because it is a realistic residue from biodegradation of soaps, and it gave a fair match for the flash points reported in the authentic F-7 sludge.[2] The composition of the surrogate is given in Table 2 (it does not include the carbonate, nitrate, and hydroxide contributions), and as can be seen from a comparison of the tables, the compositions are approximately the same.

TABLE 2 - ORNL WETF SURROGATE COMPOSITION

Constituent	Concentration (μg/g)
Aluminum	45,000
Barium	600
Cadmium	54
Calcium	270,000
Chloride	680
Chromium	470
Copper	1,270
Iron	14,300
Lead	280
Magnesium	9,400
Nickel	1,300
Oil and Grease	15,000
Organic Carbon	1,033
Phenol	200
Phosphorous	3,000
Sodium	21,000
Molybedenum	1,600
Dried Yeast	62,700

The simulated WETF sluge in Table 2 was fabricated from a "Metals Spike Solution", a "Dry Mix Blend", and other organic additives. The recipes and procedure for making the surrogate are given in Attachment A. The resulting sludge had a 71.1% water loss and a pH of 8.5, which was very similar to the actual sludge. These recipes and procedures will be used to fabricate the surrogate for the runs at DESE. The only deviations from the recipes and procedure will be that cerium (III) carbonate will be used for the uranium substitute as opposed to molybdenum and magnesium oxide will be used for magnesium carbonate. Molybdenum is usually more volatile, while the cerium will remain in the glass, which is normally the case with uranium. Magnesium oxide is being used to avoid the costs and procurement problems associated with large quantities of analytical grade magnesium carbonate. W. D. Bostick of ORNL, who formulated the surrogate composition, has agreed that these will be suitable substitutes. He suggested using a carbonate form of cerium, since the pure metal is inflammable under normal atmospheric conditions and the oxides readily hydrolyze.[8]

Glass Forming Additive

For the runs made at DESE, hydrous borax and a silica source will be used as the glass forming additives. The intent of the addition is to replicate the composition of the 28 wt% waste loaded glass vitrified by R. D. Peters of PNL. The composition of this glass is given in Table 3.[7] The major differences between his glasses and the glasses that will be produced by DESE are that cerium will be used as the uranium substitute instead of La_2O_3 and the choice of "frit" additives.

TABLE 3 - PNL 28WT% WETF WASTE LOADED GLASS

Oxide	Weight %
Al_2O_3	14.22
B_2O_3	8.83
BaO	0.18
CaO	33.26
CdO	0.18
Cr_2O_3	0.26
La_2O_3	0.21
Na_2O	15.90
NiO	0.26
PbO	0.18
SiO_2	26.49
ZnO	0.02

Test Strategy

The Stir-Melter will be used for two melter campaigns. These campaigns will test two different glass compositions. A mixture of simulated sludge and glass forming additives with a composition similar to that given in Table 4 will be tested for these campaigns. This composition represents a 45 wt% waste loading with borax and a silica source additive. Crucible tests will be performed by SRTC to define the two composition which will be run in the melter.

TABLE 4 - ESTIMATED ORNL WETF GLASS COMPOSITION

Oxide	Weight % Range
Al_2O_3	10.5 - 12.5
B_2O_3	16.0 - 17.0
BaO	0.05 - 0.07
CaO	26.0 - 27.0
CdO	0.003 - 0.004
Ce_2O_3	0.16 - 0.17
Cr_2O_3	0.005 - 0.006
Fe_2O_3	1.50 - 2.50
K_2O	1.10 - 2.00
MgO	1.05 - 1.20
MnO_2	0.03 - 0.05
Na_2O	10.0 - 11.0
NiO	0.10 - 0.30
P_2O_5	0.80 - 1.30
PbO	0.04 - 0.10
SiO_2	27.0 - 28.5
TiO_2	0.02 - 0.04
ZnO	0.20 - 0.50
ZrO_2	0.003 - 0.005

The objective of the run(s) will be to test the glass composition to assure that the Land Disposal Requirements for listed wastes have been met. These limits are given in Table 5 and are per the Code of Federal Regulation (40 CFR 268), revised July 1, 1992.

TABLE 5 - LAND DISPOSAL RESTRICTIONS

Waste Code	RCRA Regulated Metal	LDR Limit (mg/L)
D004	Arsenic	5.000
D005	Barium	100.000
D006	Cadmium	1.000
D007	Chromium	5.000
D008	Lead	5.000
D009	Mercury	0.200
D010	Selenium	5.700
D011	Silver	5.000
F006 - F009	Cadmium	0.066
F006 - F009	Chromium	5.200
F006 - F009	Lead	0.510
F006 - F009	Nickel	0.320
F006 - F009	Silver	0.072

Each campaign should require approximately 30 hours of operating time, not including warmup periods. The main objectives of these campaigns will be to develop a wasteform capable of passing the TCLP and to determine the optimum operating conditions and process limits. The melt rates will be recorded on a mass of feed and glass product per hour basis. When the melters reach steady-state operating conditions, samples will be taken. Steady-state operating conditions occur after the volume of glass produced is greater than the melter tank volume.

TASK DEFINITION

CUSTOMER IDENTIFICATION

The customer for this task is the Glass Technology Group (GTG) of the SRTC. The information obtained during this work will be used to help determine the feasibility of using vitrification as an alternative method of disposal for ORNL WETF sludge. Offgas analyses will focus on percentage of melter feed entrained and volatilized as well as the products of organic combustion.

TASK OBJECTIVES

The objective of this task is to characterize the process behavior and glass product formed upon vitrification of simulated ORNL WETF sludge. The off-gasses generated from the production runs will also be characterized to help further develop vitrification processes for mixed and low level wastes.

The tasks are individually identified as follows:

1. Vitrify feeds composed of simulated ORNL WETF sludge.
2. Determine the material balance for all compounds around the melter systems.
3. Characterize the offgas products of the simulated WETF sludge vitrification process (solids, volatile metals and products of organic combustion).
4. Obtain information on power requirements per pound of glass produced.
5. Characterize the secondary streams produced during processing.
6. Perform the TCLP on the simulated waste feed and glass product.
7. Perform the PCT on the glass product.
8. Analyze the glass product chemically for cations.
9. Obtain information on melter solids buildup.
10. Obtain electrode and melter corrosion data.
11. Obtain information on waste volume reduction.

TASK QUALITY ASSURANCE

This Section details the quality assurance measures and procedures which will be used to control the task.

The Environmental Systems Engineering Quality Assurance Manual[9] and the approved Quality Assurance Matrix will be used to provide guidance throughout the performance of the task. Additional guidance will be provided by Kathy Mottel, who is the QA representative for the GTG of the SRTC, and the SRTC Quality Assurance Department, as necessary. The general policy of the laboratory will be to emphasize quality activities and prevent quality problems. All personnel assigned to the task will be provided documentation describing the Environmental Systems Engineering QA Manual and will refer to it as necessary. Chemicals and equipment used in performing the task will be of the highest quality. Instrumentation used will have the proper controls and documentation. Research notebooks documenting the progress of the task will be controlled through standard operating procedures. Finally, the Department Quality Control Coordinator of the Department of Environmental Systems Engineering will monitor compliance with QA procedures and guidelines through audits and inspections.

A Quality Assurance Matrix, written by the GTG, will be approved by the GTG Manager, the SRTC Technical Representative, the DESE Quality Control Coordiantor, and the WSRC SCUREF QA Representative before any work is initiated on this task.

TASK DOCUMENTATION

The results of the task will be documented in a formal report jointly written by CU and WSRC personnel and, after appropriate technical review, it will be issued as a WSRC report. After release by WSRC and DOE, those portions which do not discuss proprietary equipment or processes may be released to the public per general conditions of the contract. A copy of this report will be included in the records package for the melter campaigns.

For documentation purposes, the melter runs will be identified by a three letter acronym, where the first two letters stand for the site where the sludge came from, and the third letter indicates the run number for that sludge (e.g. OR1, OR2).

At the completion of the task, a Records Package will be developed by CU. This package will be sufficiently complete so that the campaigns can be independently reconstructed, if necessary. The Records Package will contain, at least, the following:

(1) A record index, listing all contents of and number of pages in the records package. Each page of documentation shall be consecutively numbered.

(2) A copy of the requirements document (SCUREF Task Order #121).

(3) A copy of the SCUREF Technical Task Plan and this document.

(4) The SCUREF Quality Assurance Task Plan and the Quality Assurance Matrix.

(5) Original documents, or authenticated copies, of procedures actually used during the campaign which would be necessary to reproduce the results of the campaign, including equipment description.

(6) Original documents, or authenticated copies, of operating logs, laboratory notebooks, and other documents used to routinely record the progress of the campaign.

(7) Working copies of procedures (operational and analytical) used in the campaign.

(8) Copies of the outside laboratories' contracts and/or purchase orders, as well as all qualifications of the personnel involved in performing the required analyses. Information on the calibration of equipment and standards used in performing the analyses should be included with all of the results submitted in the records package.

(9) Hard copies of all analytical and process data used in preparing the final summary report.

(10) Copies of summary reports of the results of the campaign.

(11) Copies of computerized data gathered during the operations, including both computer versions and paper copies.

(12) A copy of the qualification records for the CU, WSRC, and other personnel involved in the task.

(13) Copies of SRTC surveillances and associated corrective actions.

(14) At the conclusion of the campaign, two copies of the records package will be transmitted to the SRS for storage. One copy will be provided to the WSRC SCUREF representative as a contract copy. The second copy will be retained by the Glass Technology Group as a working copy. Both complete copies of the Records Package will be forwarded to the SRTC at the SRS.

TASK RESPONSIBILITIES

Department of Environmental Systems Engineering

The Department of Environmental Systems Engineering at CU is responsible for:

- understanding and complying with the requirements of the activity as outlined in this document,

- operating the melter facility in accordance with the proper technical guidance and approved procedures. This includes operation of equipment, logging of essential data, and acquisition of process samples,

- maintaining the general facility and ensuring that all Measurement and Test Equipment (M&TE) is properly calibrated,

- notifying the SRTC Technical Representative of any conditions that would prevent compliance with the stated requirements, and

- documenting work on a routine basis in a notebook, record book, and/or report.

Clemson University Task Leader

The responsibilities of the CU Task Leader will be as follows:

- The Task Leader is the operating officer responsible for coordination of the effort and assignment of specific tasks for melter operations to either CU or WSRC employees or their subcontractors. Generally at least one WSRC representative will be permitted access to provide technical oversite and assist operations.

- ensuring that the task is conducted with the appropriate level of control (as defined in the Task QA Plan and Matrix),

- ensuring that all personnel are properly trained and that their qualifications are well documented,

- identifying the customer, the customer's requirements, and the task deliverables,

- ensuring that all documents necessary for the task are prepared and approved,

- providing the opportunity for customer review and approval of any task document, and

- maintaining activity records in accordance with QA Procedures.

SRTC Technical Representative

The SRTC Technical Representative is responsible for:

- approval of the this document, including the Task QA Plan Section, and the Quality Assurance Matrix

- assisting CU in execution of the task plan by providing engineering and technical review,

- assisting CU in providing engineering and technical assistance as it is verbally requested and as it is available, and

- providing or arranging for on-site SRTC representation during periods of operation, as deemed necessary.

SRTC Cognizant Quality Function

The SRTC Cognizant Quality Function is responsible for:

- approval of the Quality Assurance Matrix.

- review and approval of DESE subcontractors,

- performing surveillances of DESE.

Sampling

The Department of Environmental Systems Engineering is responsible for sampling of the system according to the "Run Sample Schedule". This sample schedule will indicate at which location and at what time in the processing a particular sample should be taken. This sampling schedule will also indicate the type of analyses requested and the number of replicates required. The sampling schedule is provided as Attachment B. The official sampling schedule will be issued prior to the campaign start and is subject to modification (by mutual consent of the Task Leader and the SRTC Technical Representative) during the course of the campaign.

Sample Handling

Each process sample will be logged into the "Sample Log Book". An example of how any particular process sample would be logged is shown in Figure 1. The sample will be logged by the sample name and number, the date and time that the sample was taken, the initials of the sampling operator, the analytical code requested, and any comments/observations that the operator and/or researcher might have about the sample.

SAMPLE NUMBER	DATE (MO/DA)	TIME (24 HR)	ANALYTICAL CODE(S)	INITIAL	COMMENT: description of sample
OR1-SLDG-0123	9/5	0900	SLUDGE	LAC	SLUDGE Sample . . . repeat analyses 3 times.
OR1-FEED-0124	9/6	1000	SLUDGE	MFB	FEED compositon adjusted, repeat analyses 3 times.

Figure 1. Simulated ORNL WETF Sludge Vitrification Sample Logging

A sample label with corresponding information, as shown in Figure 2, is placed on each sample bottle and the sample is transported to the proper analytical laboratory for analyses.

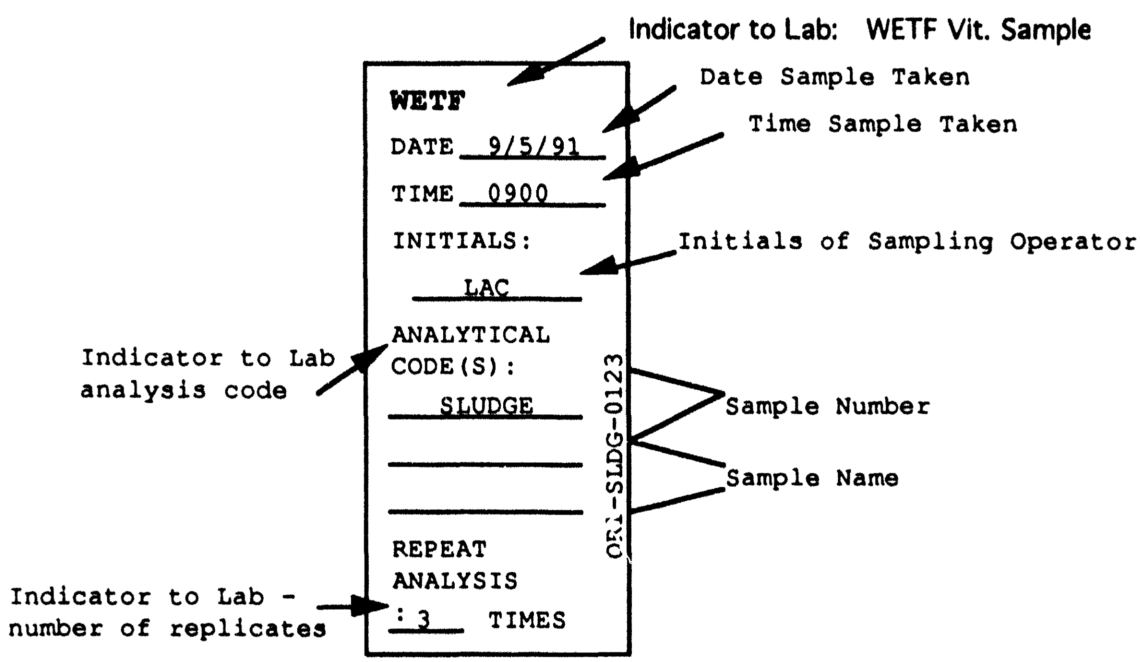

Figure 2. Simulated ORNL WETF Sludge Vitrification Sample Labeling

All samples will be identified by a four-letter acronym and a four-digit number and will be logged in sequential numerical order. The four-letter acronym will signify when and where the sample was taken during the process operation. The presently defined sample names are listed as follows:

FEED MATERIALS:

SLDG	SLUDGE, FEED COMPOSITION NOT ADJUSTED
FEED	FEED COMPOSITION, ADJUSTED

MELTER & OFF-GAS SYSTEM:

GLAS	- GLASS PRODUCT
MELT	MOLTEN GLASS FROM MELT POOL
OFFG	DIRECT OFFGAS SAMPLE
OGDP	OFFGAS DEPOSIT
COND	SCRUB SOLUTION/CONDENSATE
EXHT	OFFGAS AFTER CONDENSATION/SCRUBBING

OTHER:

SPEC	SPECIAL SAMPLES NOT COVERED BY ABOVE NAMES

The analyses required for the samples will be identified by a six-letter acronym. The six-letter acronym will signify what analyses and digestion methods are required. The presently defined analytical codes are listed as follows:

ANALYTICAL CODES

SLUDGE	ICP and AA analyses with an appropriate dissolution, IC and TCLP.
PHSLDG	pH of the sludge material
SPGRAV	Specific gravity, g/cc
WTLOSS	Percent weight loss on heating to 600°C
WT%SOL	The total weight percent solids of the simulated sludge or feed
ARCHIV	Archive sample to be stored until approval of final run report.
VOLUME	Volume of feed in melter tank
GLASSC	ICP and AA analyses with an appropriate dissolution. These determinations are to be performed in triplicate on the glass products and/or melt pool samples from each run.
GLASSD	X-ray diffraction on the glass product.
GLASSG	Glow discharge analysis on the glass product.
GLASSX	X-ray fluorescence on the glass product.
GLASSP	The PCT will be performed on the glass product from each run to determine the leaching characteristics.
GLASST	TCLP will be performed on the glass product from each run to determine the leaching characteristics.
MOLITH	Monolithic samples for subsequent leach testing.
FE2FE3	The redox ratio of the glass produced
OFFGAS	EPA Modified Method 5 train will be used to capture the offgas particles. Analyses will be performed on the offgas products.
CASCAD	Cascade impactor tests
METH5P	EPA Method 5 particulate analysis.
MET5VM	EPA Modified Method 5 volatile metals sample train
OFFNOX	Offgas analyses for NO_x emissions
OFFXRD	X-ray diffraction of the offgas products
OGVOST	EPA volatile organics
OGMMST	Off gas multiple metals sample train
ORSATG	ORSAT gas analysis
SEMVOL	Modified EPA Method 5 Semivolatile organics
TNKSOL	Tank solids build-up will be analyzed by SRTC.

Analytical Measurements

Scoping analyses will be performed by the Department of Environmental Systems Engineering under the guidance of the Environmental Systems Engineering Quality Assurance Manual.[9] Scoping analyses will be used when rapid results are needed for test modifications or when an estimate of results is necessary. For the most part, CU will not perform analyses for "publishable" results; however, if these analyses are performed by CU, QA guidelines from the Environmental Systems Engineering Quality Assurance Manual[9] and the SCUREF QA Requirements will be followed.

When applicable, SRS analytical methods will be applied.

Written procedures will be used for sample preparations and analyses. In all cases, good laboratory practices, including QA documentation, will be followed during both sample preparation and analysis.

- Appropriate fresh reagents, chemicals, reference standards, and appropriately calibrated gauges, and instruments will be used.
- Standard reference materials or reference standards will be used to calibrate all measuring equipment. These standards will be checked against standards traceable to or through unbroken chains to National Institute of Science and Technology (NIST) (or other national reference) Standards.
- Certain laboratory instrumentation, operated by approved users, will be controlled to ensure the quality of the results obtained from these instruments.

When data are needed for "publishable" results, an outside laboratory will be used. The purchase order or contract agreement with this laboratory will be a Level 1 (or equivalent quality level) procurement. This laboratory will be required to follow the same QA guidelines for analytical methods and data reporting as CU. A chain of custody form will accompany all samples submitted to outside laboratories for analyses. This chain of custody form basically identifies the sample and the places it has been and needs to be, along with the analyses required by the laboratory.

The quality of the analytical results will be controlled to ensure that only the most accurate data are reported. To do this, the accuracy and precision of all data will be determined. Control charts and tests on outlying results will be performed, and if it is decided to reject data, the reasons will be well documented.

TASK OBJECTIVES

The following section provides a summary of each of the task objectives. In each case, the importance of the objective is summarized and the means by which the objective will be achieved is explained.

1. Vitrify feeds composed of simulated ORNL WETF sludge.

As stated earlier, campaigns will be performed to prove that WETF simulated sludge can be vitrified to form a durable and leach resistant wasteform. Waste sludge simulant and glass forming additives will be used as the raw materials. At least one campaign will be performed in the Stir-Melter, additional campaigns will be run as necessary to ensure that the best glass has been produced from a durability, leach resistant, and waste loading perspective.

2. Determine the material balance for all compounds around the melter systems.

A material balance will be conducted for all compounds (elemental, ionic) in the Melter System. Samples of the waste sludge simulant will be digested and analyzed by ICP, AA, IC, and ISE methods or other suitable methods, in accordance with the sample schedule. In addition, process samples will be taken at various stages in the vitrification processing according to the Run Sample Schedule (Attachment B). The final glass product samples will also be digested by an appropriate dissolution method and analyzed by ICP, or Glow Discharge (GD), and X-ray Fluorescence (XRF) as applicable. The methods used will be in accordance with SRS procedure.

The carbon content of the glass product will also be determined. The samples will be analyzed by digestion and total carbon analyzer, or other acceptable methods for total carbon content. Depending on the analytical equipment used, organic and inorganic fractions may be available.

3. Characterize the offgas products of the simulated WETF sludge vitrification process.

The particulate matter from the offgas system will be collected by a capture train, if available, in accordance with EPA Method 5 or equivalent. Offgas particulate analysis will be performed using ICP and/or X-ray diffraction and total particulate emissions will be determined, as applicable.

The semi-volatile organics from the offgas system will be determined by EPA Modified Method 5 (GC/MS) or an equivalent method. Volatile metals within the offgas will be determined by analysis of the scrubber solutions and offgas train deposits (when available). These samples will be analyzed by ICP and/or GC/MS. The main pollutants will be reported, and other volatiles will be checked as necessary.

This information will also be used to determine the overall mass balance of the system.

Source test cascade impactor analysis will be conducted, if available, to determine the particle size distribution of the offgas. Attempts will be made to utilize standard sampling head arrangements typical of cascade impactors. In the event that direct, in-stack sampling is not feasible (due to the small diameter offgas pipes), the impactor will be fitted with a sampling nozzle and external heaters, and operated outside of the offgas duct. This will simulate the isothermal conditions of the in-stack sampling, while still operating on an isokinetic sampling basis.

4. **Obtain information on power requirements per pound of glass produced.**

A logbook will be used to record the voltage, current, and resistance while the melters are operating. This information in conjunction with the amount of glass produced will be used to determine the power requirements per pound of glass produced.

5. **Characterize the secondary streams produced during processing.**

When applicable, analyze the condensate tank and exhaust gas for cations and anions. Record volume per unit of feed material, and pH of condensate. Chain of custody forms will be used for samples submitted to EPA recognized laboratories.

6. **Perform the TCLP on the simulated waste feed and glass product.**

TCLP analysis will be conducted on unprocessed waste sludge simulant for determination of baseline leaching characteristics for characteristic metals as regulated by the EPA. Approximately three analyses will be performed on the waste sludge simulant. The TCLP will also be performed on the glass product to determine the stability of the product. TCLP RCRA metals and release of B, Si, and Ni will be monitored. Sodium releases will be monitored when extraction agents that don't contain sodium are used. The performance of the RCRA metals will be compared to the established Land Ban Restrictions and used as criteria for final disposal of the glass. An EPA recognized lab will perform the TCLP analyses to ensure the accuracy of the results. Chain of custody forms will be filled out and retained for TCLP samples.

7. **Perform the PCT on the glass product.**

The Product Consistency Test will be performed by SRTC or a certified laboratory on the glass produced. The normalized releases for RCRA materials, B, Na, Si, and Ni will be reported. This information will be useful for final disposal of the glass.

8. Analyze the glass product chemically for cations.

The glass product will be chemically analyzed for cation species. ICP and AA using appropriate dissolution methods will be used to analyze for the cations.

9. Obtain information on melter solids buildup.

At the end of the WETF sludge vitrification campaign, the stirred tank melter will be drained and any buildup of material on the melter will be documented. No rebuild of the stirred tank melter is anticipated. Any unusual accumulations will be sampled and submitted to the SRTC Technical Representative for analyses.

10. Obtain electrode and melter corrosion data.

This will be monitored at the same time as the melter solids buildup. For the stirred melter, attacked areas will be sampled. All corrosion samples will be submitted to the SRTC Technical Representative for analyses. Any signs of electrode or melter corrosion or impeller erosion should be documented and reported to SRS.

11. Obtain information on waste volume reduction.

Complete records of the amount of simulated sludge and glass forming additive used for each run will be documented. The weight percent solids and specific gravity of the feed for each run will also be recorded. This information will be used to calculate sludge content from liters to dry weight, since waste loading and glass compositions are calculated on a dry weight basis. In addition, melting conditions, such as operating temperature, will also be documented. This information will be used to determine the waste reduction capabilities. Melt rates will be recorded. Large monolithic samples will be obtained, where possible, for future testing.

REFERENCES -

1. Federal Register, "Land Disposal Restrictions for Third Scheduled Wastes, Final Rule," 55 FR 22627 (June 1, 1990).

2. Memorandum from W. D. Bostick to D. F. Bickford, "Recipe for surrogate Y-12 WETF Sludge", May 28, 1993.

3. Memorandum from W. D. Bostick to D. F. Bickford, "Preliminary Data for Y-12 WETF Tank F-9 Sludge", June 3, 1993.

4. Memonrandum from W. D. Bostick to D. F. Bickford, "X-ray Diffraction of Dried WETF Tank F-9 Sludge", June 4, 1993.

5. G. N. Greaves, N. T. Barrett, G. M. Antonini, F. R. Thornley, B. T. M. Willis, and A. Steel, "Glancing-Angle X-ray Absorption Spectroscopy of Corroded Borosilicate Glass Surfaces Containing Uranium," **J. Am. Chem., Soc., 111**, 4313-4324 (1989).

6. D. F. Bickford, M. E. Smith, J. P. Faraci, **"Program Plan: DWPF Stirred Melter Development,"** WSRC-RP-91-0419 (April 8, 1991).

7. Memorandum from R.N. Peters to C. A. Cicero, "Simulated WETF Glasses Fabricated by PNL", July 6, 1993.

8. Memorandum from W. D. Bostick to C. A. Cicero and D. F. Bickford, "Surrogate(s) for U in Simulated WETF Sludge", July 13, 1993.

9. Environmental Systems Engineering of Clemson University, **Quality Assurance Manual**, Version 1.0 (July 1, 1993)

Attachment A

Recipes and Procedure for Mixing ORNL WETF Surrogate

METALS SPIKE SOLUTION
Recipe for 1 Kg

Constituent	Amount Added
$Cr(NO_3)_3*9H_2O$ FW = 400	7.200 g
$Cd(C_2H_3O_2)_2*2H_2O$ FW = 266.5	0.253 g
$Cu(C_2H_3O_2)_2*2H_2O$ FW = 199.6	8.000 g
$Pb(C_2H_3O_2)_2*3H_2O$ FW = 379.4	1.030 g
$Ni(NO_3)_2*6H_2O$ FW = 290.8	12.900 g
$UO_2(NO_3)_2*6H_2O$ FW = 502.2	6.730 g
or	or
$Na_3MO_4*2H_2O$ FW = 242	8.070 g
or	or
$Ce_2(CO_3)_3$ FW = 410.2	5.497 g
0.1 N HCl	Balance of 1 Kg

DRY MIX BLEND
Recipe for 1 Kg

Constituent	Amount Added
$Al(OH)_3$ FW = 78	130.00 g
Fe_2O_3 FW = 159.7	20.40 g
$Na_2HPO_4*7H_2O$ FW = 268.1	25.90 g
$NaHCO_3$ FW = 84	61.00 g
$CaCO_3$ FW = 100.1	666.00 g
$MgCO_3$ FW = 84.3	32.60 g
$Ba(OH)_2*8H_2O$ FW = 315.5	1.38 g
Dry Yeast Powder	62.70 g

PROCEDURE FOR MIXING SURROGATE

To prepare one kilogram of surrogate ORNL WETF sludge, the following steps should be followed:

1. Add 150 g "Metals Spike Solution" to approximately 200 g H_2O

2. Add 0.2 g phenol (C_6H_5OH)

3. Alternately add 300 g of "Dry Mix Blend" and the remainder of the water required to yield a final mass of 1,000 g. When approximately half of these materials have been added, add 1.3 g of dodecane (flash point 160°F). Add the remainder of the dry blend and water.

4. Adjust the slurry pH value (using HCl or $Ca(OH)_2$) to a value between 8.7 - 9.1. NOTE: Past batches have required 4.7 g $Ca(OH)_2$ to raise the pH from 7.6 to 8.5.

Attachment B

Run Sample Schedule

Material	Description	Analytic Code	#Samples	#Replicates*
SLDG	Simulated WETF	SLUDGE	3	1
	sludge	SPGRAV	3	1
		WTLOSS	3	1
		WT%SOL	3	1
		PHSLDG	3	1
		ARCHIV	3	1
FEED	Melter feed	SLUDGE	3	1
		WTLOSS	3	1
		WT%SOL	3	1
		SPGRAV	3	1
		VOLUME	5**	1
		ARCHIV	3	1
GLAS	Glass produced	GLASSC	3	1
		MOLITH	as possible	3
		GLASSL	2	3
		ARCHIV	5	1
		FE2FE3	3	1
		GLASSX	3	1
OFFG	Direct offgas	OFFGAS	as possible	1
	sample (EPA	METH5P	as possible	1
	Methods)	OGMMST	as possible	1
		CASCAD	as possible	1
OGDP	Offgas deposit	OFFXRD	as possible	1
COND	Scrub solution/	OFFGAS	as possible	1
	condensate	OGMMST	as possible	1
EXHT	Offgas sample	METH5P	as necessary	1
	after scrubbing/	OGVOST	as necessary	1
	condensation	OFFGAS	as necessary	1
SPEC	Any special	TNKSOL	as needed	1
	samples needed			
	which are not			
	covered above			

*The number of replicates refers to the number of times that an analyses is to be performed. For example, a sludge material will be sampled three different times and separately digested and analyzed.

**An initial volume measurement is to be taken, as well as four other volume measurements during melting. The time that these samples are taken should be recorded, so that the melt rate with time can be determined.

Distribution:

WSRC: E.W. Holtzscheiter, 773-A
E.F. Duhn, 773-A
M.J. Plodinec, 773-A
D.A. Crowley, 704-1T
L.F. Landon, 704-T
C.T. Randall, 704-T
M.K. Andrews, 773-A
D.F. Bickford, 773-A
C.A. Cicero, 773-A
C.M. Jantzen, 773-A
K.E. Mottel, 773-42A
B.J. Skwarek, 773-42A
P.E. Lowe, 773-42A
R.C. Young, 773-42A
G.S. Bumgarner, 773-41A
B.D. Helton, 773-41A
K. Imrich, 773-A
J.C. Marra, 773-A
A.L. Kielpinski, 773-11A
J. Whitehouse, 786-6A
Glass Technology Group (14)
TIM, 703-43A (4)

CU: D.M. Bennert, DESE
T.J. Overcamp, DESE
J.L. Resce, DESE

ORNL: Jan Berry
Bill Bostick

Other distribution to be provided by Westinghouse Savannah River Company

DATE FILMED

5/20/94

END