1 of 1

ROCKY FLATS PLANT PRECIPITATE SLUDGE SURROGATE VITRIFICATION DEMONSTRATION

by

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CLEMSON UNIVERSITY
DEPARTMENT OF ENVIRONMENTAL SYSTEMS
ENGINEERING
TECHNICAL TASK PLAN

ROCKY FLATS PLANT
PRECIPITATE SLUDGE SURROGATE
VITRIFICATION DEMONSTRATION (U)

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Attachment A: Run Sample Schedule

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
RCRA:	Resource Conservation and Recovery Act
RFP:	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
TRU:	Transuranic
XRD:	X-ray Diffraction
XRF:	X-ray Fluorescence
WSRC:	Westinghouse Savannah River Company

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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 EPA¹, 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 of 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 Rocky Flats Plant's (RFP) precipitate sludge is considered one of these representative wastes. It is inorganic, with less than 1% organic concentration, and has associated EPA waste codes of F001, F002, and F005A. The uniqueness of this sludge is that it contains a large amount of nitrates, which when processed require additional offgas controls. Presently, the current inventory is approximately 3 m³. An alternative wasteform is needed since the waste is currently stored in 55 gallon drums, 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 nitrates and waste water treatment sludges containing small amounts of filter aid.

RFP PRECIPITATE SLUDGE DESCRIPTION

The RFP precipitate sludge originates from treatment (chemical precipitation) of aqueous waste from plutonium recovery operations, and thus is a transuranic (TRU) waste. Four different wastes are generated from this process, but the sludge to be tested can be considered either first or second stage sludge. The first stage of the solidification operation is a chemical precipitation of radioactive elements from the liquid wastes. The chemicals used in the precipitation are ferric sulfate, calcium chloride, magnesium sulfate, and coagulants. The resulting sludge is concentrated using a filter press coated with diatomaceous earth filter aid. A thin layer of this filter cake is continuously cut from the drum filter, which produces a wet sludge with a water content of up to 60%, and an effective waste loading of about 40% sludge. The usual operating practice was to add about 0.5 Kg of portland cement/diatomaceous earth blend to each 55-gal drum of sludge to control free water. Portland cement was added to some of the drums to absorb any free liquids. The effluent from this first stage of precipitation was filtered and sent to the second stage batch process where it was mixed with high nitrate radioactive wastes. The second stage sludge was treated using the same chemical precipitation steps as before, and then packed in drums with cement. The plutonium content of the first stage sludge is about 15 times that of the second stage material.²

Plutonium is the primary isotope of concern in the waste stream. The average Pu content in an historic inventory of RFP first stage sludge was on the order of 340 $\mu\text{g/g}$, wet weight basis.² The sludge also contains small amounts of chromium, nickel, lead, cadmium, and silver. From a regulatory perspective, this means that it contains solvents or compounds to make it a F001, F002, and F005A Resource Conservation and Recovery Act (RCRA) waste.³

An analysis of RFP precipitate sludge was performed and a surrogate composition was developed. The surrogate composition based on a dry basis is given in Table 1.⁴ The radioactive elements were not included in the composition because of the small quantities present. The surrogate simulates the bulk physical and chemical properties of the RFP precipitate sludge.

The sludge surrogate was spiked with elevated levels of EPA regulated heavy metals. The main purpose of this spike was to see how the glasses produced from the surrogate would perform on the TCLP under the different operating parameters with the associated levels of RCRA metals. The metals concentration of the simulated sludge as compared to the actual sludge is given in Table 2.⁴

TABLE 1 - RFP PRECIPITATE SLUDGE SURROGATE COMPOSITION

Compound	Weight (g)
CaSO ₄ *2H ₂ O	967
Fe(OH) ₃	777
Mg(OH) ₂	317
NaNO ₃	237
Diatomaceous Earth	207

TABLE 2 - METALS CONCENTRATION IN RFP PRECIPITATE SLUDGE

Metal	Surrogate Sludge (ppm)	Actual Sludge (ppm) ⁵
Chromium	500	54 to 481
Nickel	500	No data
Lead	500	29 to 250
Cadmium	500	4.6 to 13.0
Silver	500	56 to 189

By further breaking down the dried basis composition (assuming that RFP uses the same diatomaceous earth as Clemson will) and combining the metals spike concentration, a RFP precipitate sludge surrogate oxide composition was determined. The oxide composition is given in Table 3. The oxide composition is helpful when trying to develop glass compositions, since it is assumed that all of the elements convert to an oxide state in glass.

TABLE 3 - RFP PRECIPITATE SLUDGE SURROGATE OXIDE COMPOSITION

Oxide	Weight %
Ag ₂ O	0.065
Al ₂ O ₃	0.646
CaO	15.156
CdO	0.069
Cr ₂ O ₃	0.088
Fe ₂ O ₃	56.024
MgO	10.557
Na ₂ O	8.303
NiO	0.077
PbO	0.065
SiO ₂	8.951
Total	100.000

Vitrification and subsequent delisting of RFP precipitate 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 is a high density, leach resistant, robust waste form.
- Glass has a very high potential for being delisted, due to the toxicity reduction, 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.
- 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.

Microwave solidification research performed on a laboratory scale by G.S. Sprenger and V.G. Eschen of RFP with the RFP precipitate sludge surrogate given in Table 1 and the metals spike concentration given in Table 2 was successful in producing sixteen glass compositions. Their studies concentrated on the effects of glass forming additives, waste loading, melt temperature, and quench rate on the final glass product.⁴

Diatomaceous earth and borax, in various amounts, were used by Sprenger and Eschen as the glass forming additives with waste loadings varying from 25 to 75 wt%. The glasses were melted at 950, 1075, or 1200°C and quenched at a slow, medium, or fast rate. The vitrified material was removed from the melting container and fractured to collect a representative sample for TCLP analysis. Approximately 50 gram subsamples were used for the TCLP extractions. TCLP results indicated that all of the glasses fell below the F006 limit for chromium, one exceeded the nickel F006 limit, several exceeded the lead and silver F006 limits (high waste loaded glasses), and all exceeded the cadmium F006 limit.⁴ Though these glasses did exceed the TCLP limits, it must be taken into account that the metals were present in much higher amounts than expected in the actual waste (as can be seen in Table 2). When the TCLP results were averaged based on the different operating parameters, it was shown that waste loading was the most critical operating parameter affecting leachability. It was also shown that higher borax concentrations in the glass forming additive resulted in higher leachability.⁴

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.

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

Precipitate Sludge Surrogate

As mentioned earlier, the RFP precipitate sludge was analyzed and a surrogate composition was developed by RFP personnel. W. D. Bostick of Oak Ridge National Laboratory (ORNL), used RFP's surrogate composition to develop the recipe to be used by the MWIP. The recipe based on a wet and dry basis is given in Table 4.⁷ This recipe, along with a metals spike equivalent to that used by RFP in their microwave studies (see Table 2), will be used to fabricate the surrogate for the runs at DESE. In order to simulate the effects of Pu in the actual sludge, a Ce concentration of 500 ppm will be added to the sludge in the form of cerium (III) carbonate. The only deviation from the recipe will be that Fe₂O₃ will be used instead of Fe(OH)₃. Fe₂O₃ is being used because of availability. The substitution should not affect the overall processing. Bostick stated that it would be permissible to add less water to the sludge, since this would simulate the insertion of a pre-pelletizing drying process.⁷ Accurate records of how much water is added will be maintained by DESE when making the surrogate.

TABLE 4 - MWIP RFP PRECIPITATE SLUDGE SURROGATE COMPOSITION

Compound	Wet Basis Weight %	Dry Basis Weight %
CaSO ₄	22.4	34.6
Fe(OH) ₃	17.9	27.7
Mg(OH) ₂	7.4	11.5
NaNO ₃	12.4	18.5
Diatom. Earth	4.9	7.7
Water	35.0	N/A

A comparison of the two surrogates (Table 1 versus Table 4) shows that RFP's surrogate is higher in Fe(OH)₃, Mg(OH)₂, and diatomaceous earth and lower in CaSO₄ and NaNO₃ based on a weight % basis. The oxide composition for the MWIP surrogate, using the RFP suggested surrogate spike and the composition of Clemson's diatomaceous earth, is given in Table 5. This table when compared to Table 3 better reflects the difference in the two compositions. The biggest difference between the two surrogates is that RFP's surrogate has more Fe₂O₃, while MWIP's surrogate contains more Na₂O, which is expected since the batch recipes also had this relation.

PROCESSING NOTE: When CaSO₄ is mixed with water, it will set up to form "Plaster of Paris". Precautions must be taken to avoid this from happening.

TABLE 5 - MWIP RFP PRECIPITATE SLUDGE SURROGATE OXIDE COMPOSITION

Oxide	Weight %
Ag ₂ O	0.060
Al ₂ O ₃	0.555
CaO	21.501
CdO	0.063
Ce ₂ O ₃	0.065
Cr ₂ O ₃	0.081
Fe ₂ O ₃	46.079
MgO	8.835
Na ₂ O	14.951
NiO	0.071
PbO	0.060
SiO ₂	7.681
Total	100.002

Glass Forming Additive

For the runs made at DESE, hydrous borax (with ten waters) and diatomaceous earth will be used as the glass forming additives. The amounts to be added were determined in crucible studies performed by Cicero and Andrews at SRTC. These crucible studies were based on compositions determined by RFP personnel in their microwave studies. RFP personnel were able to obtain a 75 wt% waste loading using a glass forming additive consisting of 20% borax and 80% diatomaceous earth and by melting at 1200°C.⁴ Two different glass compositions were determined to be the most suitable for the melters at DESE by Cicero and Andrews. For the EnVitCo melter, a feed stream of 75 wt% simulated RFP precipitate surrogate, 10% borax, and 15% diatomaceous earth was considered to produce the best glass at high temperatures. On the other hand, a feed stream of 65 wt% simulated RFP precipitate surrogate, 14% borax, and 21% diatomaceous earth was considered to produce the best glass at lower temperatures, which would apply to the stirred melter.⁸ Additions of 3 wt% charcoal should be added to each of these melter feed streams to deter the formation of a sulfate salt layer.

The intent of the glass forming additive additions was to produce a glass which had the lowest release rates on the TCLP, while achieving the highest waste loading. For the RFP glasses, cadmium concentration was the limiting factor for the SRTC crucible studies and for the RFP microwave solidification studies. Cadmium was the only RCRA metal that exceeded the LDR limits on the TCLP for two glasses in the SRTC crucible studies⁴ and for all glasses in the RFP microwave studies.⁸

Test Strategy

Two campaigns will be conducted using a mixture of simulated sludge, borax and diatomaceous earth. One campaign will be conducted using

the EnVitCo melter, and the other will use the Stir-Melter. The EnVitCo will be used for the high temperature, high waste loading glass, while the Stir-Melter will be used for the lower temperature, lower waste loading glass. When the Stir-Melter demonstration is being performed, the redox probe should be used to monitor the redox of the glass because of the effect of high redox levels on Inconel.

The objective of the runs will be to test the glass compositions to assure that the Land Disposal Requirements (LDR) for listed wastes as required by the RCRA have been met. To determine if the glasses have met this objective, they will be subjected to the TCLP. The leachability results will be compared against the TCLP and the LDR limits listed in Table 6. The LDR limits given in Table 6 are per the Code of Federal Regulation (40 CFR 268), revised July 1, 1992.

TABLE 6 - LAND DISPOSAL RESTRICTIONS

RCRA Regulated Metal	TCLP Limit (mg/L)	LDR Limit (mg/L)
Barium	100.0	N/A
Cadmium	1.0	0.066
Chromium	5.0	5.2
Lead	5.0	0.51
Nickel	N/A	0.32
Silver	5.0	0.072

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 processing 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 three times 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 RFP precipitate sludge. Offgas analyses will focus on percentage of melter feed entrained and volatilized as well as percentage of nitrate destroyed during vitrification.

TASK OBJECTIVES

The objective of this task is to characterize the process behavior and glass product formed upon vitrification of RFP precipitate sludge surrogate. The off-gases 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 RFP precipitate sludge surrogate.
2. Determine the material balance for hazardous and tracer compounds around the melter systems.
3. Characterize the offgas products of the RFP precipitate sludge surrogate vitrification process (solids, volatile metals and NO_x).
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 sludge surrogate 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 Manual⁹, the approved Quality Assurance Task Plan, and the approved Quality Assurance Matrix will be used to provide guidance throughout the performance of the task. Additional guidance will be provided by the SRTC Quality Assurance Department and Kathy Mottel, who is the QA representative for the GTG of the SRTC, 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.

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. RF1, RF2).

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 oversight and assist operations.
- ensuring that the task is conducted with the appropriate level of control (as defined in the QA Task Plan and the QA 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,
- 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 Task Plan and Quality Assurance Matrix,
- review and approval of DESE subcontractors, and
- 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 A. 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
RF1-SLDG-0123	9/5	0900	SLUDGE	LAC	SLUDGE Sample . . . repeat analyses 3 times.
RF1-FEED-0124	9/6	1000	SLUDGE	MFB	FEED compositon adjusted, repeat analyses 3 times.

Figure 1. RFP Sludge Precipitate Surrogate 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.

Indicator to Lab: RFP Vit. Sample

Date Sample Taken

Time Sample Taken

Initials of Sampling Operator

Indicator to Lab analysis code

Sample Number

Sample Name

Indicator to Lab - number of replicates

RFP
DATE 9/5/93
TIME 0900
INITIALS:
LAC
ANALYTICAL
CODE(S):
SLUDGE

REPEAT
ANALYSIS
:3 TIMES

RF1-SLDG-0123

Figure 2. RFP Precipitate Sludge Surrogate 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
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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	PCT will be performed on the glass product from each run to determine the durability.
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
CASCAD	Cascade impactor tests
METH5P	EPA Method 5 particulate analysis
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 Manual⁹, the SCUREF QA Requirements, and the Quality Assurance Matrix 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 is needed for "publishable" results, an outside laboratory will be used. The purchase order or contract agreement with this laboratory will be of a level equivalent to or better than the QA program of CU. 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 is 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 RFP precipitate sludge surrogate.

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

2. Determine the material balance for hazardous and tracer compounds around the melter systems.

A material balance will be conducted for 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 A). The final glass product samples will also be digested by an appropriate dissolution method and analyzed by ICP and AA, or Glow Discharge (GD), and X-ray Fluorescence (XRF). The methods used will be in accordance with SRS procedure.

3. Characterize the offgas products of the RFP precipitate sludge surrogate vitrification process.

The particulate matter from the offgas system will be collected by a capture train 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.

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. 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 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.

Since nitrates are being used in the sludge surrogate, the formation of NO_x is anticipated. Offgas sampling by EPA methods will be used to determine the amount of NO_x evolved from the melter.

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 sludge surrogate feed and glass product.

TCLP analysis will be conducted on unprocessed sludge surrogate for determination of baseline leaching characteristics for characteristic metals as regulated by the EPA. Approximately three analyses will be performed on the sludge surrogate. The TCLP will also be performed on the glass product to determine the stability of the product. TCLP RCRA metals and release of B and Si 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, and Si 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 RFP precipitate sludge surrogate vitrification campaign, any buildup of material on the cold top melter components will be documented after tearing down the melter and before rebuilding it. A similar investigation will be conducted with the stirred tank melter, though this will be limited to drainage of the tank and observation. No rebuild of the stirred tank melter is anticipated. Any unusual accumulations will be sampled and submitted to the SRTC Technical Representative for analyses. The SRTC Technical Representative has the option to delay the teardown/rebuild of the melter in the event that further research has been initiated. If no further research is anticipated, the rebuild of the melter will take place in preparation for other programs.

10. Obtain electrode and melter corrosion data.

This will be monitored at the same time as the melter solids buildup. The wear and attack on the cold top melter components will be documented before the melter is rebuilt. 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 sludge surrogate 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.

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3. G. S. Sprenger and V. G. Eschen, "Critical Operating Parameters for Microwave Solidification of Hydroxide Sludge," in A. Moghissi et al. (eds.), Proceedings of the Second International Symposium on Mixed Waste, Baltimore, MD, August 17-20, 1993, pp 7.1.1-7.1.5.
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8. C. A. Cicero and M. K. Andrews, **"Simulated RFP Precipitate Sludge Crucible Studies,"** WSRC-TR-94-00107 (May 24, 1994).
9. Environmental Systems Engineering of Clemson University, **Quality Assurance Manual**, Version 1.0 (July 1, 1993)

Attachment A
Run Sample Schedule

Material	Description	Analytic Code	#Samples	#Replicates*
SLDG	RFP Precipitate	SLUDGE	3	1
	sludge surrogate	SPGRAV	3	1
		WTLOSS	3	1
		WT% SOL	3	1
		PHSLDG	3	1
		GLASST	2	3
		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
		GLASST	2	3
		GLASSP	2	3
		ARCHIV	5	1
		FE2FE3	10	1
		GLASSX	3	1
OFFG	Direct offgas	CASCAD	2	1
	sample (EPA	METH5P	2	1
	Methods)	OGMMST	2	1
OGDP	Offgas deposit	OFFXRD	2	1
COND	Scrub solution/ condensate	OGMMST	as possible	1
EXHT	Offgas sample	METH5P	1	1
	after scrubbing/ condensation	OGVOST	1	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.

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