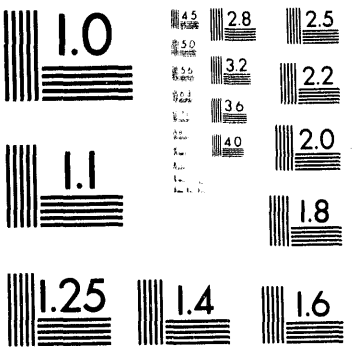
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ANALYTICAL STUDY PLAN: SHIELDED CELLS BATCH 1 CAMPAIGN (U)

by
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DOE Contract No. **DE-AC09-89SR18035**

DISCLAIMER

WESTINGHOUSE SAVANNAH RIVER COMPANY
SAVANNAH RIVER TECHNOLOGY CENTER

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ANALYTICAL STUDY PLAN: SHIELDED CELLS BATCH 1 CAMPAIGN (U)

INTRODUCTION AND SUMMARY

Radioactive operations in the Defense Waste Processing Facility (DWPF) will require that the Savannah River Technology Center (SRTC) perform analyses and special studies with actual Savannah River Site (SRS) high-level waste sludge. SRS Tank 42 and Tank 51 will comprise the first batch of sludge to be processed in the DWPF. Approximately 25 liters of sludge from each of these tanks will be characterized and processed in the Shielded Cells of SRTC.

During the campaign, all of the processes that will be performed with radioactive sludge will be performed in the Shielded Cells by Shielded Cells Operations (SCO) personnel. These processes include sludge characterization, sludge washing, rheology determination, mixing, hydrogen evolution, feed preparation, and vitrification of the waste. To complete the campaign, the glass will be characterized to determine its durability and crystallinity. A task plan for this campaign has been written.[1] The campaign will be directed by the Task Team: N. E. Bibler, B. C. Ha, M. S. Hay, D. M. Ferrara, and M. K. Andrews.

The success of the campaign depends almost entirely on the support of the Analytical Development Section (ADS). Nearly 300 samples will be generated in this campaign, with up to nine different types of analyses for each sample. More than 95% of these analyses will be performed by ADS personnel. The analytical methods used should be similar to those that will be used in the DWPF Analytical Laboratory.[2]

The purpose of this document is to describe the types of samples that will be produced during the campaign, the sampling schedule and analyses required for each type of sample, and the methods for sample and analytical control. This campaign will follow the DWPF Sample Schedule[3] and the Extended Sludge Processing Schedule.[4] Attachment 1 describes the analyses required for each study. In addition, the expected number of samples and the number of replicates per sample are included. These estimated numbers are provided to ADS to allow for planning. The exact number of samples and number of replicates per sample will be determined by the researcher based on the importance of the sample.

TYPE OF SAMPLES

This campaign will produce three general types of samples that will require a variety of analyses: slurries, solids and aqueous solutions. All of the samples will be radioactive and will be generated in the Shielded Cells. The various types of samples are described in detail below.

Slurry Samples

There will be six types of slurry samples during the campaign: as received sludge slurries, washed sludge slurries, mixed slurries, hydrogen evolution slurries, sludge-precipitate hydrolysis aqueous (PHA) slurries, and sludge-PHA-frit slurries.

Solid Samples

Two types of solid samples will be analyzed. These will be samples of glass and any residues that may be obtained from the melter or the off-gas system.

Aqueous Solution Samples

There will be three types of aqueous solutions submitted for analyses. One will be the supernates of the various slurries. The second type will be the aqueous solutions resulting from the application of the Product Consistency Test (PCT)[5] leach test to the radioactive glasses. The third type will be solutions resulting from the melter off-gas system, including condensate and bubbler solutions.

SAMPLE SCHEDULE & ANALYSES REQUIRED FOR SLURRY SAMPLES

Analyses requested for the six types of slurries will be similar in that each slurry will be analyzed for its nonradioactive and radioactive elemental composition. Tables 1 and 2, respectively, show the elements and radionuclides required for analysis. Additional analyses listed in Attachment 1 will be required

depending on the specific type of slurry. To establish the accuracy of the sampling technique, three slurry samples will be taken for crucial analyses as indicated in Attachment 1. Each sample will be analyzed one time, unless indicated otherwise. When the Task Team determines it necessary, a glass standard will be dissolved and analyzed concurrently with the samples. More details can be found elsewhere.[6]

Table 1: Elements Required for Slurry Analyses[3,7]

Ag	K	Rh
Al	La	Ru
B	Li	Si
Ba	Mg	Sn
Ca	Mn	Sr
Cd	Mo	Th
Co	Na	Ti
Cr	Ni	U
Cu	P	V
Fe	Pb	Zn
Hg	Pd	Zr

Table 2: Radionuclides Required by the DWPF Sample Schedule[3]

Ni-59	Sn-126	Np-237
Co-60	Cs-135	Pu-238
Ni-63	Cs-137	Pu-239
Se-79	Ce-144	Pu-240
Sr-90	Pm-147	Pu-241
Zr-93	Sm-151	Pu-242
Nb-93	Eu-154	Am-241
Tc-99	Th-230	Am-243
Ru-106	U -234	Cm-244
Pd-107	U -238	

As Received Sludge Slurries

Chemical and radiochemical analyses required by the DWPF analytical sample schedule and by the Waste Acceptance Preliminary Specifications (WAPS), will be performed on the Tank 42 sludge to determine the elements present for DWPF process control and product reporting requirements. Analyses for these samples are important since they will be used to establish the baseline composition of the Tank 42 radioactive sludge. Results of the analyses of the soluble salts in the as-received supernate will be reviewed to judge how much washing will be necessary.

Washed Sludge Slurries

Prototypical washing operations will be performed in the Shielded Cells using Tank 42 sludge. This will provide Waste Management with an early warning of potential problems and a determination of the efficiency of washing (i.e. identification of the probable endpoint and the likely number of cycles required). Samples will be taken after washing to determine the composition of the sludge.

Mixed Sludge Slurries
Sludge from Tanks 42 and 51 will be combined in the same proportions as DWPF Batch 1. After the slurries have been mixed, samples will be taken to identify any problems, such as gross segregation, encountered during blending. The distribution of radionuclides will also be determined.

Hydrogen Evolution Slurries
The Tank 42 sludge will be processed in a small glass Sludge Receipt and Adjustment Tank (SRAT) to determine the hydrogen generation from the noble metal catalyzed decomposition of formic acid. Samples of the combined Tank 42 and 51 (Batch 1) sludge will also be run. During the experiments, H_2 and NH_3 will be monitored using a gas chromatograph. Samples of the SRAT product will be analyzed by ADS.

Sludge-PHA Slurries
These samples will be taken after the sludge and PHA have been processed in the larger scale SRAT in the Shielded Cells. Analyses of these samples will be used to determine if processing in the SRAT affected the slurry composition (including radionuclides) and to determine the amount and type of frit to add to the waste so that it may be vitrified.

Sludge-PHA-Frit Slurries
Samples of this material will be taken to confirm that the slurry is suitable to feed to the melter. Since the composition of this slurry must be known prior to feeding the melter, these analyses must have a turnaround time of four days. If remediation is required, the slurry will again be sampled and analyzed.

SAMPLE SCHEDULE & ANALYSES REQUIRED FOR SOLID SAMPLES

The two types of solid samples generated will be glass samples and residues from the melter off-gas system.

Glass Samples
Four types of glass samples will be taken during the campaign. Samples of glass will be taken directly from the pour stream of the melter, from a vitrified melter feed tank sample, and from selected cans after they are filled by the slurry-fed melter. A fully-loaded glass will also be made and analyzed.

Pour Stream Samples
Samples from the melter pour stream will be taken periodically while the melter is being fed. These samples will be taken to determine the composition of the glass in the pour stream as a function of time and to determine if noble metals and actinides settled while the melter was idling. The concentration of the major radioactive and nonradioactive elements in the glass will be measured.

Vitrified Melter Feed Tank Samples
Samples of the melter feed will be taken from the melter feed tank and vitrified in a small high-temperature furnace. The resulting glass will be analyzed to determine the composition of the glass that will be produced from this feed and to measure the Fe(II)/Fe(Total) ratio in the glass. The glass will be analyzed to determine if the feed composition is correct and if the proper redox will be maintained in the melter.

Selected Can Samples
The melter will pour the glass into 500 ml stainless steel cans. Glass samples from selected cans will be taken and submitted for analyses for the elements and radionuclides listed in Tables 1 and 2. A standard glass will be analyzed simultaneously to establish the accuracy of the analyses. Part of these samples of glass will also be examined by scanning electron and optical microscopy to determine if they contain any crystalline material. If any crystalline material is found, its identity will be determined by X-Ray Diffraction (XRD), if the glass is not too radioactive.

Fully-Loaded Glass
Radioactive PHA will be combined with radioactive sludge from Tank 42. An appropriate frit will be added, and the slurry will be vitrified in a muffle furnace. The fully-loaded glass will be analyzed to determine its composition. The glass will also be subjected to the PCT.

Off-Gas Residue Samples
Attempts will be made to sample any solid residues that collect in the off-gas system of the melter. These residues will be examined by Scanning Electron Microscopy (SEM) and possibly XRD to qualitatively determine their composition. They will also be analyzed by counting techniques to determine the radionuclides present. Attempts will be made to dissolve the solids and analyze the resulting solution to further determine their composition.

SAMPLE SCHEDULE & ANALYSES REQUIRED FOR AQUEOUS SAMPLES

The three types of aqueous solution samples will be the supernates from the slurries, solutions from the melter off-gas system, and leachates from the PCT.

Supernate Samples
The solutions from the slurries will be sampled and analyzed to determine their compositions and pH values. Samples of the as-received supernate will be analyzed prior to significant rinse water addition. If possible, three samples of the supernate will be taken after each washing step to determine if further washing is required.

Melter Off-Gas Solution Samples

Two types of aqueous solutions will result from the operation of the melter off-gas line. These are the off-gas condensate solution and bubbler solutions. The condensate results from the condensation of the water fed to the melter with the waste/frit slurry. Bubbler solutions result from samplers put on the off-gas line to trap any particulates that are in the off-gas itself. During the campaign, up to ten bubbler and ten condensate samples will be produced.

PCT Leachate Samples

Samples of the final glass will be taken from selected cans and leached according to the Product Consistency Test (PCT).[5] The PCT is a crushed glass leach test which will be used to determine the durability of the glass. The results from the Batch 1 glass will be compared to those of the Environmental Assessment (EA) glass.[8]

METHODS FOR SAMPLE CONTROL

Control of the samples is important because many samples will be generated, many individual analyses will be performed, samples will be radioactive, obtaining samples is difficult, and data from the analyses of the samples will be used for key DWPF and Tank Farm decisions. To ensure the success of the campaign, stringent sample controls will have to be exercised by GTG personnel, by SCO personnel operating the Shielded Cells, and by ADS personnel.

Sample Controls Applied by GTG and SCO Personnel

The sample controls by GTG will be similar to those for the Tank 51 Campaign.[7] The Task Team will generate a unique number for each sample. This number will be used throughout the campaign as the reference number for that specific sample. All of the samples will be radioactive and taken at appropriate process steps during the campaign by SCO personnel. The samples will be placed in bottles labeled with the appropriate reference number(s). SCO personnel should ensure that these labels are sturdy enough to withstand the chemical and radiation environment in the Shielded Cells. Many of the samples will have to be transported to Cell 8 (the analytical cell of the Shielded Cells) from Cells 1-4, where the samples are generated. In Cell 8, all sample dissolutions will occur. Titrations and pH and Fe(II)/Fe(total) measurements are the only analyses that can be performed directly in Cell 8. Consequently, nearly all of the analyses will have to be performed in the ADS laboratories in B and C-wing of 773-A. Therefore, the samples will have to be removed from the Shielded Cells and transported to GTG laboratory B-111 or to ADS Sample Receiving. (The task team is responsible for specifying which samples are transferred directly to ADS Sample Receiving.) In B-111, aliquots will be removed from the sample for each requested analysis. After the aliquots are properly surveyed by Health Protection personnel, the samples will be delivered to ADS Sample Receiving. Samples will be retained until all analyses are complete.

Sample Controls Applied by ADS

Sample or aliquot control by ADS will be greatly simplified because of the controls already exercised by GTG. Each sample submitted by the Task Team will already have the unique sample number. A second number will be obtained by entering the samples and analyses requested into the Laboratory Information Management System (LIMS) of ADS. The appropriate number assigned by the Task Team for each sample will also be recorded in the LIMS. ADS must track what analyses have been completed on each sample and whether the results have been reported. Each aliquot will be retained until the results of the analyses have been reported to and accepted by the Task Team. Final results of each analysis will be recorded in the LIMS using the appropriate ADS number. After the results have been reported and accepted for an analysis, the remainder of that specific aliquot can be discarded by ADS personnel using appropriate methods. A hard copy of the sample results will be retained by the Task Team as a record of the task. For certain analyses, such as the sludge-PHA-frit slurries and the organics, the turnaround time will be critical: four days for the frit slurries and five days for the organics.

METHODS FOR ANALYTICAL CONTROL

Analytical controls will be especially important because most of the data generated by the campaign will be used in the DWPF Waste Form Qualification Reports. Analytical controls, as discussed below, will be applied primarily by ADS since ADS will be performing the analyses.

For analytical control, all analyses will be performed by qualified ADS personnel. Documentation shall exist which indicates the specific qualifications of each person performing the analysis. Good laboratory practices, including QA documentation, will be followed at all stages of analytical work. Instruments shall be properly calibrated with standards traceable to one of the WSRC accepted standards. Documentation shall be available that verifies that the calibrations are correct and that the shelf life of the standards has not expired. All documentation shall be available if requested by GTG or the Quality Section (QS) of SRTC. The Quality Section of SRTC will perform surveillances of ADS to ensure that all documentation is in place and to ensure proper application of controls.

All analyses will be performed by ADS personnel using procedures that have been approved by ADS Management for application at SRS. The precision and accuracy of the results should be comparable to that cited for the procedure.[9] The Task Team will submit blind standards to be analyzed concurrently with critical samples to check the accuracy of the analyses. The critical samples will be those for determining the composition of the sludge slurries and the glasses. A standard glass (with a certified analysis) of composition similar to the sludge or glass being analyzed will be dissolved and analyzed identically to the sample. A high aluminum

glass (HM) or a depleted uranium glass will be used. The results for the standard shall agree with the certified analysis within the precision of the analytical method. The results of the samples will be checked by attempting to close the material balance calculations.

ATTACHMENTS

Attachment 1 - Required Analyses for the Batch 1 Campaign

REFERENCES

[1] M. K. Andrews, "Research and Development Plan: Shielded Cells Batch 1 Campaign (U)," WSRC-RD-92-07, Rev.2, (1993).

[2] C. J. Coleman, "DWPF Analytical Procedures," DPST-88-270, (1988).

[3] M. L. Mertz, "Transmittal of Revised DWPF Sample Schedule (U)," OPS-DTC-910022, Rev. 1, (1992).

[4] E. D. Lee, "Extended Sludge Processing Sampling and Analytical Requirements Revision 1 (U)," WER-ITP-920029, (1992).

[5] C. M. Jantzen, N. E. Bibler, D. C. Beam, W. G. Ramsey and B. J. Waters, "Nuclear Waste Glass Product Consistency Test (PCT) - Version 5.0 (U)," WSRC-TR-90-539, Rev. 2, (1992).

[6] C. J. Coleman and R. A. Dewberry, "SRTC Analytical Task Plan for DWPF Waste Compliance Analyses (U)," WSRC-TR-92-369, (1992).

[7] N. E. Bibler, "Analytical Study Plan: Shielded Cells Tank 51 Campaign (U)," WSRC-RD-91-10, Rev. 0, (1991).

[8] U.S. Department of Energy , "Environmental Assessment Waste Form Selection for SRP High-Level Waste," USDOE Report DOE-EA-0179 (1982).

[9] C. J. Coleman, "Basic Data Report: Precision and Accuracy of DWPF Analytical Methods," WSRC-RP-89-764, (1989).

APPROVALS

M. John Plodinec — GTG MANAGER — DATE 10/4/93

M.A. Rochkind for PFC — ADS REPRESENTATIVE — DATE 10/5/93

Attachment 1
Required Analyses for the Batch 1 Campaign

Study	Description	#Samples*	#Reps/sample*	Required Analysis
Chemical Composition	As Received Slurry	3	1	Elemental ** Radionuclides *** pH Total Solids Soluble Solids Density Free Hydroxide TOC TIC Carbonate Fluoride Chloride Nitrate Nitrite Sulfate Formate Oxalate Phosphate U U-233 U-235 Am Am-242m Cm Cm-243 Cm-245 Cm-247 Pu Np NH3 Total Gamma Rheology
Washing	Supernate During Wash Cycle	3/wash	1	Elemental ** Radionuclides *** pH Soluble solids Insoluble solids Density Free Hydroxide Carbonate Nitrate Nitrite Sulfate Oxalate Phosphate Fluoride Chloride Sr-90 Cs-137

Attachment 1
Required Analyses for the Batch 1 Campaign

Study	Description	#Samples*	#Reps/sample*	Required Analysis
				U Pu Np Cm Am Total Gamma
	Washed Sludge Slurry	3	1	Elemental ** Radionuclides *** pH Total Solids Soluble Solids Density Free Hydroxide Total Hydroxide Carbonate Yield Stress Nitrate Nitrite Sulfate Formate Phosphate Fluoride Chloride Loss on Calcining NH3 U U-233 U-235 Am Am-242m Cm Cm-243 Cm-245 Cm-247 Pu Np Sr
Mixing	Mixed Sludge Slurry	3	1	Elemental ** Radionuclides *** pH Total Solids Soluble Solids Density Free Hydroxide Total Hydroxide Carbonate Yield Stress Nitrate Nitrite

Attachment 1
Required Analyses for the Batch 1 Campaign

Study	Description	#Samples*	#Reps/sample*	Required Analysis
				Sulfate Formate Phosphate Fluoride Chloride Loss on Calcining NH3 U U-233 U-235 Am Am-242m Cm Cm-243 Cm-245 Cm-247 Pu Np Sr
Hydrogen Production	Slurry Product	3	1	Elemental ** Radionuclides *** TIC Carbonate Nitrate Nitrite Sulfate Formate
Feed Prep	Blended Feed (sludge + PHA)	3	1	Elemental ** Radionuclides *** pH Total Solids Insoluble solids Density Nitrate Nitrite Sulfate Formate Fluoride Chloride Loss on Calcining NH3
	SME Product (sludge + PHA +frit)	3	1	Elemental ** Radionuclides *** pH Total Solids Insoluble solids Density TOC TIC

Attachment 1
Required Analyses for the Batch 1 Campaign

Study	Description	#Samples*	#Reps/sample*	Required Analysis
				Fluoride Chloride Nitrate Nitrite Sulfate Formate NH3 Alpha PHA Gamma PHA
MFT Sample	Glass	3	1	Elemental ** Radionuclides *** Fe2+/Total Fe
Pour Stream	Glass	6	1	Elemental ** Radionuclides ***
Selected Cans	Glass	1	2	Elemental ** Radionuclides *** SEM XRD
Fully-Loaded Glass	Glass	1	2	Elemental ** Radionuclides *** Fe2+/Total Fe
Off-gas Residue	Solid	2	1	Elemental ** Radionuclides *** SEM
PCT	Aqueous sol'n	20	3	Radionuclides *** pH Sodium Boron Lithium Potassium Silicon Aluminum Iron Manganese Magnesium Calcium Nickel Fluoride Chloride Nitrate Nitrite Sulfate
Off-Gas	Aqueous sol'n	3	1	Elemental ** pH Soluble Solids Insoluble Solids TOC Nitrate Nitrite

Attachment 1
Required Analyses for the Batch 1 Campaign

Study	Description	#Samples*	#Reps/sample*	Required Analysis
				Sulfate
				Formate
				Fluoride
				Chloride
				U
				Pu
				Sr-90
				Tc-99
				Ru-106
				Cs-137

* The number of samples and the number of replicates/sample are only an estimate. The exact number will be determined by the researcher based on the importance of the sample.

** All elements listed: (Ag, Al, B, Ba, Ca, Cd, Co, Cr, Cu, Fe, Hg, K, La, Li, Mg, Mn, Mo, Na, Ni, P, Pb, Pd, Rh, Ru, Si, S , Sr, Th, Ti, U, V, Zn, and Zr)

*** Radionuclides:

Ni-59	Zr-93	Sn-126	Sm-151	U-238	Pu-241
Co-60	Nb-93	Cs-135	Eu-154	Np-237	Pu-242
Ni-63	Tc-99	Cs-137	Eu-155	Pu-238	Am-241
Se-79	Ru-106	Ce-144	Th-230	Pu-239	Am-243
Sr-90	Pd-107	Pm-147	U-234	Pu-240	Cm-244

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