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Hanford Supplemental Waste Processing Technologies – Fiscal Year 2003 Recommendations for Selective Dissolution Studies and Radioactive Waste Sample Preparation

G. B. Josephson
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Prepared for the U.S. Department of Energy
under Contract DE-AC06-76RL01830

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Executive Summary

This document describes two tasks that support CH2M Hill Hanford Group's (CH2M HILL) initiative to test and demonstrate/deploy supplemental treatment technologies. While the testing and demonstrations of the supplemental technologies is to be accomplished by private vendors selected through a competitive Request for Proposals (RFP), the two tasks discussed here are not part of the vendor's scope. The two tasks are:

1) preparing radioactive waste samples for vendor testing by removing radionuclides and particulates
2) addressing technical issues associated with dissolving and retrieving waste from tanks.

The DOE (through Hanford contractors) will provide decontaminated samples of radioactive waste for vendor testing, and this document describes the specific details for the preparation of these radioactive waste samples.

CH2M HILL is also responsible for retrieving saltcake waste from the single-shell tanks. They expect to dissolve the waste using water dissolution. When water dissolves the waste, the more soluble components of the waste will dissolve first. The initial saltcake liquid solution removed from the tank will include the soluble cesium and these other dissolved salts, leaving the lesser soluble components of the waste in the tank. This phenomenon, termed selective dissolution, is expected to provide a partial separation of cesium from the waste. This document describes a program involving tank dissolution demonstrations, modeling, and laboratory testing to more completely understand how the composition of the retrieved saltcake waste will change during the course of retrieval.

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1.0 Introduction

In August 2002 the U.S. Department of Energy (DOE) issued a *Performance Management Plan for Accelerated Cleanup of the Hanford Site* (available at: http://www.hanford.gov/docs/rl-2002-47/rl-2002-47.pdf). The goal of the accelerated schedule described by DOE is to "accelerate tank waste treatment completion by 20 years, accelerate risk reduction, and save $20 billion." To achieve this goal all tank waste treatment at Hanford must be completed by 2028, which will require a significant increase in the processing rate of the baseline Waste Treatment Plant (WTP). One approach to increasing the processing rate is to conduct supplemental processing external to the WTP. CH2M Hill Hanford Group, Inc. (CH2M HILL) is supporting Hanford mission acceleration by conducting an aggressive testing and demonstration program of technology options to provide supplemental processing capacity for saltcake waste in sixty-eight of the Hanford single-shell tanks (SSTs).

The testing and demonstration of the supplemental technologies is to be accomplished by private vendors selected through a competitive Request for Proposals (RFP). Earlier in 2002, Pacific Northwest National Laboratory (PNNL) issued recommendations for the testing that need to be accomplished to provide data for an informed selection of the technology(ies) to be further developed, leading to full-scale demonstration and deployment (Josephson et al. 2002). That report identified testing that should be conducted on simulants and actual Hanford waste samples. This memorandum is a companion to that report and recommends how some of the actual waste samples for vendor testing should be prepared so that they may, in turn, be provided to the vendors (see Section.3).

In 2002 CH2M HILL issued "Recommendation for Supplemental Technologies for Potential Mission Acceleration" (Gasper et al. 2002). That report described CH2M HILL's recommendations of the technologies to quickly demonstrate and deploy in order to provide supplemental tank waste treatment capacity. The recommendations included using "selective dissolution" to remove the waste from the tanks. The selective dissolution concept, noted in Gasper et al. (2002), is based upon removing the more soluble chemical and radionuclide species (e.g., cesium and technetium) preferentially in the first water volumes added to the SSTs to promote saltcake dissolution and retrieval. The cesium rich stream could be transferred to the double-shell tanks (DST) for subsequent processing in the WTP and the remaining SST waste would have lower radioactivity during supplemental processing. The Hanford Performance Management Plan includes a milestone to test selective dissolution as a supplemental pretreatment by August 2003. The major activities to evaluate selective dissolution include the dissolution/retrieval demonstration planned for tank 241-U-107 (U-107) and the retrieval demonstration on 241-S-112 (S-112). This memorandum contains recommendations of a modeling and laboratory-testing program to support analysis of data obtained from the waste tank demonstrations (Section 2), which may employ different water addition methods (e.g., sprinkler or localized additions). Through development of modeling tools and laboratory data, the results of the U-107 and S-112 demonstrations should aid in the prediction of the waste composition profiles during retrieval of the saltcake contained in the 68 tanks identified in supplemental treatment technologies initiative documents.

2.0 Selective Dissolution – Laboratory Studies and Modeling

Experimental dissolution studies of Hanford saltcake waste samples, including those from Tanks U-107 and S-112, indicate that significant variations in composition during the retrieval of saltcake waste are likely (Herting 2001; Herting and Bechtold 2002). The studies represent one of several possible "idealized" dissolution and retrieval processes. In these stepwise dissolution tests, water or other diluent is added to a waste sample, mixed thoroughly, allowed to equilibrate, and after centrifugation, a majority of the free liquid is removed. The process is repeated with fresh diluent and the retrieved liquid samples are subsequently analyzed for chemical constituents and radionuclides. Predominantly soluble species such as cesium ion (Cs), pertechnetate (TcO_4^-, the soluble form of technetium, Tc), and nitrite are shown to be "retrieved" relatively early in the stepwise process while the bulk of other less soluble species, including sulfate and phosphate, tend to remain in the waste sample container until later in the dissolution/retrieval process. Successfully taking advantage of compositional variation during in-tank dissolution to reduce pretreatment steps required following waste retrieval and, thereby, enhancing waste processing rates, is a selective dissolution process.

To better understand the likely outcome of tank-scale selective dissolution processes, a modeling project is recommended [as part of the fiscal year (FY) 2003 supplemental treatment technologies initiative activities] to complement DOE-Office of Science and Technology (OST) funded university laboratory studies. The project seeks to answer two primary questions:

1) Is selective dissolution a predictable and controllable process to remove a significant fraction of Cs and Tc radionuclides from the retrieved saltcake waste? In theory a relatively small volume of Cs- and Tc-rich waste could be retrieved for disposition in the WTP and the larger volume of waste would be directed to the supplemental waste treatment train to accelerate tank closure.

2) How will the composition of the waste change during retrieval and for different water addition methods? For example, selective dissolution might be used to concentrate sulfate in a relatively small volume of retrieved waste to minimize the impact on waste loading in vitrified waste.

Tables 2.1 and 2.2 identify the specific laboratory testing and modeling activities considered important to help answer these questions. Table 2.1 consists of activities recommended for implementation in FY 2003, and Table 2.2 includes related activities worthy of future consideration. The tables are organized principally by the Technical Issues/Uncertainties identified and discussed by selective dissolution workshop attendees on August 29 and September 3, 2002. Specific testing, analysis, and/or modeling activities considered important to address each issue are shown in additional columns. Table 2.3 summarizes recommendations for maximizing the information relevant to selective dissolution obtained during the dissolution and retrieval of Hanford waste tanks, particularly U-107 and S-112.

To assess whether any selective dissolution process will be successful, a sound fundamental understanding of the waste dissolution chemistry is needed as a foundation (e.g., the Herting studies). Complete chemical thermodynamic equilibrium models (e.g., ESP for Hanford waste species), validated against actual waste data, allow estimation of composition for other waste systems where equilibrium conditions are attained or are assumed. However, because the tanks are not well mixed and diluent will be added non-uniformly (i.e., not volumetrically uniform), the composition will vary in the tank. Furthermore, the flow of diluent and dissolved salt solution within the porous saltcake structure (eventually reaching the salt-well screen) will also be complex. Given these complexities, there is a need to expand from laboratory stepwise contact tests and equilibrium chemistry models to larger-scale dissolution studies and hydrodynamic models tracking local dissolution/precipitation chemistry to predict what might occur on the tank scale. Models could range in complexity from relatively simple calculations combining equilibrium chemistry with mass transport to sophisticated models that directly couple waste species thermodynamics (e.g., ESP model) with multi-dimensional porous media transport (e.g., STOMP model). Modeling efforts should emphasize developing the simplest models that deliver practical results.

Selective dissolution laboratory testing and modeling activities are an important compliment to, not a substitute for, the information potentially available from actual tank dissolution and retrieval operations such as are planned for tanks U-107 and S-112 in FY 2003. We need to take full advantage of the data available from these and other full-scale retrieval opportunities, as they are perhaps our best test beds to know how selective dissolution processes will work. This is the basis of the recommendations given in Table 2.3. A goal of the laboratory-scale testing and modeling activities shown in Table 2.1 is to make a case that the tank-scale results from U-107 and S-112 dissolution and retrieval processes are understandable and predictable.

Information gained in the studies identified in Tables 2.1, 2.2, and 2.3 will benefit retrieval of the 68 saltcake SSTs (Gasper et al. 2002) and downstream processing of the retrieved waste – whether or not selective dissolution is a component of a process for Cs and Tc removal supporting a Waste Incidental to Reprocessing (WIR) designation. The studies seek to improve our understanding of the waste tank physical and chemical conditions prior to and during retrieval and to develop modeling tools to estimate the time-phased composition of dissolved and retrieved liquid waste.

Table 2.1. Selective Dissolution Test Recommendations for FY 2003

Technical Issue / Uncertainty	**Requirements Objective**	**Specific Testing**	**Test Size, Actual Waste or Simulant,** Basis for Selection
Collect data to assess partitioning in actual waste samples for comparison to in situ dissolution/retrieval (e.g., U-107 and S-112).	To what extent does tank dissolution and retrieval behave "ideally" (e.g., stepwise dissolution tests and ESP equilibrium model predictions)?	Obtain important data during tank dissolution/retrieval operations (see Table 2.3 for recommendations).	See Table 2.3.
		Assess U-107 (and S-112) retrieval data (e.g., NO3/NO2 ratio gives indication of interstitial vs. dissolution liquid removed) obtained from monitoring systems (i.e., in-line Raman spectroscopy and gamma probes) and grab sample analyses.	Paper study - review of tank process testing data. This activity exists within the scope of the S-112 retrieval program, but a comparable one is not specifically identified for U-107.
	Resource: Optimize Mississippi State University - Diagnostic Instrumentation and Analysis Laboratory (MSU-DIAL) activities for DOE-OST in FY 2003 to support.	MSU-DIAL: Complete additional ESP modeling as warranted to assess the results of U-107 and S-112 dissolution/retrieval. (MSU-DIAL completed some ESP modeling for U-107. ESP-based multi-step dissolution/retrieval modeling was completed for S-112 and is currently being completed for U-107 at PNNL.)	Paper studies. Retrieved liquid composition estimated from model of thermodynamic equilibrium between waste and added diluent based on batch contacting. NOTE: This limited model does not capture temporal variation in composition, effects of incomplete equilibration, or address the hydrodynamics of tank-scale retrieval.
Collect data to assess different water addition methods and locations and dilution/retrieval protocols.	Resource: Optimize Florida International University (FIU) testing activities for DOE-OST in FY 2003 to support.	Engineering-scale column or tank tests with simulants to determine the effects of different water addition methods and locations and dilution/retrieval protocols on selective dissolution behavior. Homogeneous simulant.	Engineering-scale columns or tanks (e.g., ≥1-ft diameter and >1-ft deep). Assumes suitable simulant available.
		Develop suitable physicochemical saltcake simulants.	Paper study and laboratory-scale development effort

Technical Issue / Uncertainty	**Requirements Objective**	**Specific Testing**	**Test Size, Actual Waste or Simulant,** Basis for Selection
Collect data to assess impacts of compositional variation and heterogeneities within a tank on selective dissolution/retrieval.	Resource: Optimize FIU testing activities for DOE-OST in FY 2003 to support.	Engineering-scale column or tank tests with simulants including 2-D heterogeneities (layered or axial). Develop suitable physicochemical saltcake simulants.	Engineering-scale columns or tanks (e.g., ≥1-ft diameter and >1-ft deep). Assumes suitable simulant available. Paper study and laboratory-scale development effort
Collect fundamental equilibrium chemistry data to enhance performance and predictive capability of thermodynamic models (e.g., ESP code).	Resource: Optimize MSU-DIAL activities for DOE-OST in FY 2003 to support. Is the sodium nitrate/phosphate ternary system properly represented in ESP? ESP model may under-predict nitrate and nitrite solubilities at high hydroxyl and aluminum concentrations. (This condition is expected to be rare in tank dissolution/retrieval operations.) Other specific chemical systems?	Laboratory chemical thermodynamics experiments on important and less understood chemical systems. (May already be part of MSU-DIAL workscope. Need to determine what additional testing is required in FY 2003.)	Laboratory-scale. Pure chemicals and mixtures.
Develop models (mass transport and thermodynamic) to improve predictive capabilities of retrieved waste composition during selective dissolution processes.	What would models predict for large-scale homogeneous and 2-D heterogeneous (layered or axial) saltcake waste systems?	Develop calculations or models that combine waste species solubility/chemistry information with mass transport within the saltcake waste.	Paper studies. Couple mass transport/chemical thermodynamics calculations. Calibrate and test against engineering- and tank-scale results.

Technical Issue / Uncertainty	**Requirements Objective**	**Specific Testing**	**Test Size, Actual Waste or Simulant,** Basis for Selection
	Will phosphate or carbonate dissolve and then reprecipitate and plug the flow paths? Will insoluble species plug the flow paths?	Apply models; compare to engineering-scale simulant tests and available data from saltcake-tank dissolution retrieval operations (e.g., U-107 and/or S-112).	Paper studies.
	Resource: Optimize FIU testing activities for DOE-OST in FY 2003 to support.	Conduct flow column tests and examine the composition at different places in the column.	Engineering-scale columns or tanks (e.g., ≥1-ft diameter and >1-ft deep). Simulant.
	How do the results of U-107 and S-112 dissolution/retrieval operations compare to model estimates?	Apply and tune models based on available data from U-107 and S-112 saltcake-tank dissolution retrieval operations.	Paper studies.

Table 2.2. Selective Dissolution Test Recommendations for Future Consideration

Technical Issue / Uncertainty	Requirements Objective	Specific Testing	Test Size, Actual Waste or Simulant, Basis for Selection
Collect data to assess partitioning in actual waste samples for comparison to in situ dissolution/retrieval (e.g., U-107 and S-112).	In addition to related Table 2.1 activities. To what extent does tank dissolution and retrieval behave "ideally" (e.g., stepwise dissolution tests and ESP equilibrium model predictions)?	Flow-column testing on U-107 and/or S-112 waste samples, possibly including in-line continuous Raman, to compare with stepwise dissolution tests and actual tank retrieval. Apparatus may require a vacuum system to assist flow due to capillary holdup in short column. Dissect any "plugged" column.	Laboratory small column tests (e.g., 1 to 1.5-in. diameter x >4-in. tall). Size limited by availability of actual waste samples. Develop method with simulants first, then complete actual waste tests. Stepwise dissolution tests have been completed for U-107 and S-112 (Herting 2001; Herting and Bechtold 2002).
Collect data to assess partitioning in actual waste samples of tanks that are candidates for in-situ selective dissolution/retrieval pretreatment.	Collect data on S-103, S-105, and/or S-106.	Stepwise dissolution and possibly flow-column testing (Raman spectroscopy for continuous anion monitoring would be most helpful in flow tests).	Laboratory-scale actual waste tests. Early retrieval of S-103, S-105, and S-106 identified in a recent TPA milestone.
Develop approaches to utilize chemical equilibria for advantageous selective dissolution and/or selective precipitation.	Can we modify the dissolution/retrieval program to enhance selective dissolution?	Complete experiments where the size of the stepwise water additions is reduced, as compared to earlier investigations, to assess potential analyte concentration extremes (e.g., more ideal chromatographic separation).	Laboratory-scale. Simulant first, then do an actual waste sample. If sample available, use S-112 because the standard stepwise dissolution tests have been completed (Herting and Bechtold 2002).
	Can something be added to the diluent to enhance the selective retrieval of Cs and Tc radionuclides (e.g., through selective precipitation of the species)?	Assess possible additives to promote in-tank precipitation of Cs (e.g., nickel ferrocyanide for Cs complexation) and Tc (e.g., a chemical reducing agent to reduce pertechnetate to a less soluble technetium oxide form)?	Paper studies - review reports and the pertinent literature. Possible follow on laboratory-scale studies with simulants first then actual waste samples.
	Can something be added to	Stepwise dissolution tests on a sulfate rich	Laboratory-scale. Simulant first, then do an

	the SST tank diluent (e.g., fluoride) to enhance selective retrieval of sulfate – e.g., create an in-situ sulfate separation technique? (Alternatively, consider adding the fluoride in double-shell tanks after waste is retrieved from SSTs - a selective precipitation process). Other diluents or target waste species?	waste (focus on S-112) with a diluent containing fluoride to limit sulfate solubility during the bulk of waste retrieval. Assess the possible co-precipitation of phosphate and sulfate due to fluoride addition.	actual waste sample. Use S-112, because it is relatively sulfate rich, and stepwise dissolution tests with water and another diluent have been completed (Herting and Bechtold 2002).
Collect data to assess impacts of compositional variation and heterogeneities within a tank on selective dissolution/retrieval.	In addition to related Table 2.1 activities.	Parallel plate, two-dimensional tests with simulants including “manufactured” heterogeneities (regions containing gases, e.g., hydrogen, or other permeability barrier).	2-D engineering scale (e.g., >1 ft width and height) "ant farm". Assumes suitable simulant available.
		Three-dimensional column or engineering-scale tank tests with simulants including 3-D heterogeneities (e.g., heterogeneous region(s) not distributed uniformly in layers or axially).	Engineering-scale tanks or columns (e.g., ≥1-ft diameter and >1-ft deep). Assumes suitable simulant available.
		Develop suitable physicochemical saltcake simulants.	Paper study and laboratory-scale development effort
Collect data to assess different water addition methods and locations and dilution/retrieval protocols.	In addition to related Table 2.1 activities.	Engineering-scale tests (simulants) to determine the effects of different water addition methods and locations and dilution/retrieval protocols on selective dissolution behavior. Two-dimensional parallel-plate apparatus using homogeneous and heterogeneous simulants.	2-D engineering scale (e.g., >1 ft width and height) "ant farm" and 3-D tanks or columns (e.g., 1-ft diameter and >1-ft deep).
		Develop suitable physicochemical saltcake simulants.	Paper study and laboratory-scale development effort
Collect fundamental	In addition to related Table	Update the ESP thermodynamic parameters	Paper study. May require contract with OLI

equilibrium chemistry data to enhance performance and predictive capability of thermodynamic models (e.g., ESP code).	2.1 activities.	and database as necessary. Assess data integrity.	(ESP vendor) and oversight by thermodynamics expert.
Apply models (porous media and thermodynamic) to optimize selective dissolution processes.	How can tank-scale selective dissolution be optimized?	Extend the coupled transport/chemistry model to alternative tank processing schemes to optimize selective dissolution and retrieval.	Paper studies using coupled porous media/chemical thermodynamics model.
What are the initial conditions, chemical and physical, of the 68 saltcake SSTs before dissolution/retrieval?	Chemical and physical descriptions of the tanks are needed as inputs to any selective dissolution/retrieval model.	Review and assess various tank waste databases and reports (including the results of stepwise dissolution experiments). Mine existing data.	Paper study.
	What is the current distribution of chemicals in tanks (radial and vertical)?	Develop a model to estimate tank concentration gradients based on fill history and tank thermal conditions. A preliminary two-dimensional model developed at PNNL in conjunction with the S-112 retrieval program predicts redistribution of solids in tanks due to chemical and thermal conditions (e.g., natural convection).	Paper study.
		Conduct lab tests with simulants to assess possible redistribution of solids in tanks due to chemical and thermal conditions (e.g., natural convection).	Engineering-scale tests with simulants.
	Why does one saltcake drain well and another poorly? Hydraulic conditions in the waste tanks are a big unknown.	Assess data and reports and develop models (e.g., porous media/chemistry and solids redistribution) to probe impacts of particle size, porosity, “Ostwald ripening,” and chemistry on hydraulic behavior. Also assess the impact of the specific evaporator that processed the waste, and consider the effects	Paper studies.

		of insolubles and sludges in the tanks.	
Assess the potential impact (e.g., variable composition) to WTP, supplemental treatment technologies initiative processes, tank farms, and waste disposal systems.	Waste feed delivery - What species are going to come out of the tanks as they dissolve them? Waste treatment system and tank closure - How do contaminants of concern (e.g., uranium, iodine or iodate, technetium, nitrate, chromium, and others) partition to the dissolved waste and what remains as residual in the tank? Waste treatment system - What will be the effect of fluoride from high concentration tanks to the waste treatment system when it is retrieved? Tank processing and systems - what off-gases could result from dissolution/retrieval processes (e.g., C-104 organics, noxious vapors; other tanks, ammonia likely)?	Apply a coupled porous media/chemical thermodynamics model with appropriate description of tank initial conditions (chemical and physical) to predict the variation in retrieved liquid composition. By difference, estimate composition of waste remaining in tank. Refinement of transport/chemistry model required, providing predictive capability of off-gas concentrations as a function of dissolution/retrieval.	Paper studies.

Table 2.3. Selective Dissolution Test Recommendations for Tank Operations

Technical Issue / Uncertainty	Requirements Objective	Specific Testing	Test Size, Basis for Selection
Collect data to assess in situ dissolution/retrieval (e.g., U-107, S-112, and other tanks).	To what extent does tank dissolution and retrieval behave "ideally" (e.g., compositions measured in stepwise dissolution tests and ESP equilibrium model predictions)? How does it compare to coupled transport/chemistry model results (e.g., Table 2.1)?	Add Raman spectroscopy (anion analysis) and gamma monitor (^{137}Cs tracking primarily) on U-107 process line. Similar in-line monitoring already planned for S-112 retrieval. (Alternatively, greatly increase the number of liquid samples analyzed during retrieval.)	Tank process testing. U-107 dissolution/retrieval test as planned (37000gal) will not be adequate to determine whether selective dissolution is occurring. Extension of U-107 retrieval has been proposed in a baseline change request.
	Extend the range of uses of and reduce the potential impact of solids on results obtained from Raman systems.	Develop a 2nd generation Raman monitor that can deal with slurries (e.g., filter a side stream).	Laboratory-scale development and testing; tank deployment. No known plans to develop this capability.
	What part of the waste mass dissolves and how does it change geometrically during dissolution/retrieval?	Additional equipment is needed to obtain topographical data during U-107 retrieval. Also, increase the number of cameras in the tank to provide more extensive view coverage and to minimize shadowing in the tank.	No known plans to add this capability. No known plans to use more than one camera in S-112 and U-107.

3.0 Radioactive Waste Sample Preparation for Supplemental Treatment Technologies[1]

Supplemental treatment technologies being considered for implementation are: 1) containerized grout, 2) bulk vitrification, 3) sulfate removal, 4) transuranic elements (TRU) solidification, and 5) pretreatment to support containerized grout or bulk vitrification. It is anticipated that testing of these technologies with actual tank waste will be performed in FY 2003. To support these tests, it will be necessary to provide actual waste samples to vendors conducting the testing. The waste for the first three technologies (containerized grout, bulk vitrification, and sulfate removal) should be representative of waste after it has been pretreated such as it would be for a full-scale demonstration. That is, suspended solids, cesium, and technetium should be removed[2]. Therefore, prior to supplying the waste to the vendors representative pretreatments should be conducted. The objective of the pretreatment is simply to decontaminate the waste sample as necessary to proceed with the vendor tests. No attempt will be made to optimize the separation processes or evaluate whether these are the optimal methods to use.

This recommendation describes the requirements for removing solids, ^{137}Cs, and ^{99}Tc from the dissolved saltcake waste samples. The waste for the TRU solidification demonstration is not anticipated to be pretreated before processing. Therefore, a representative waste sample to be supplied to TRU solidification vendors will not be pretreated other than to validate that the sample contains sufficient insoluble solids for vendor testing. The samples to be prepared and the steps to prepare the samples are described below. The steps are summarized in tabular form in Table 3.1, and further explanations of each preparation step are given in Sections 3.2-3.9.

The radioactive waste to be used in the FY 2003 for supplemental technologies testing will be taken from archive samples currently stored at 222-S. There will be three primary composite radioactive samples required:

Sample 1. Six to 12 L of dissolved saltcake feed to be provided to the grout, bulk vitrification and sulfate removal vendors--This sample will have solids filterered, Cs/Tc removed, and will be adjusted to ~5M sodium content. The prepared sample will be analyzed for shipment to the vendor.

Sample 2. TRU sludge for the TRU washing/stabilization vendors--This sample will contain at least 250 g of insoluble solids. An aliquote of the sample will be filtered to verify that the sample contains enough solids and then analyzed for shipment to the vendor.

Sample 3. Four to 8 L of dissolved saltcake to support the pretreatment (Cs/Tc ion exchange and solid-liquid separations) technology testing--This sample will be adjusted to ~5M sodium content but will not be filtered or have Cs or Tc removed. An aliquote of the sample will be analyzed to verify that the sample contains approx. 50-300 g of insoluble solids to support solid liquid separation testing.

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[1] Preparation steps may be completed at the Hanford 222-S facility or at PNNL, Radioprocessing Laboratory.

[2] Technetium separation may not be desirable for vendors testing containerized grout processes. The formulated grout needs to be tested for retention performance of waste constituents. It may be desirable to leave the typical technetium in the sample for grout formulation so that more accurate leaching data may be collected. If the technetium is too low an remains undetected in the leach testing then the leaching rates cannot be calculated for performance assessment. Similar logic could also apply to waste supplied to vitrification vendors, but glass release of technetium may be reliably estimated based upon data from WTP testing and the release of other marker constituents. The value the real data vs. data estimated from the extensive WTP database would justify the extra exposure.

Table 3.1 Summary of Sample Preparation Recommendations

Sample	**Vendors**	**Amount per vendor**	Compositing **Sec. 3.1**	**Filtration Sec. 3.3**	**Preliminary Analysis Sec.3.2**	**Cs/Tc removal Sec. 3.4,3.5**	**Adjustment to 5M Sec. 3.6**	**Final Analyses Sec. 3.7**	**Shipping preparation Sec.3.8**	**Reporting Sec. 3.9**
1	Bulk vitrification, Grout, sulfate removal	1-2L	Yes	0.45 micron dead-end filter	ICP AES for Na	Cs DF=200 Tc—DF=10 [3]	Yes	Yes; see Table 3.2	Yes	Yes
2	TRU	250g insoluble solids	Yes	No	Verify 250g insoluble solids to vendor	No	No	Yes: see Table 3.3	Yes	Yes
3	Pretreatment	2-4L w/50-300 g insoluble solids	Yes	No	ICP AES for Na; Verify 50-300 g insoluble solids to vendor	No	Yes	Yes; see Table 3.2	Yes	Yes

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[3] See Footnote 2 in Section 3.0

3.1 Sample Compositing and Analysis

Samples 1and 3will be prepared and analyzed in a similar manner. Individual archive samples (as identified by CH2M HILL) will be combined to form a composite, water will be added as needed and the mixture mixed thoroughly.

For the TRU sludge sample (Sample 2), individual archive samples (as identified by CH2M HILL) will be combined to form a composite and homogenized per existing 222-S laboratory procedures. The homogenized sample will be sub-sampled and analyzed. Table 3.3 lists the analytes to be determined and the minimum reportable quantities for these analytes. All analyzes will be performed in duplicate.

3.2 Sampling and Preliminary Analysis of Solution (Samples 1 and 3)

The "as-received" saltcake waste will be dissolved in deionized water (if not already done so) to approximately of 5M Na. A portion of the composite sample will be filtered through a 0.45 micron membrane and the clarified liquid will be analyzed by ICP-AES for sodium, IC for anions, GEA (for Cs-137), and Tc-99 (ICP-MS). The samples will be analyzed in duplicate.

3.3 Removing Suspended Solids from the Dissolved Saltcake Sample (Sample 1)

The dissolved saltcake sample will be clarified using readily available, off-the-shelf laboratory filtration systems. Depending on the volume of the feed solution, the filtration will be performed by means of a dead-end vacuum filter or by using a small in-line cartridge filter. Filters with pore size 0.45-µm or smaller will be used.

Permeate sufficient to provide the waste needs for all of the vendors (except TRU stabilization vendors) will be filtered. During the filtration the temperature of the solution passed through the dead-end filter will be maintained at 25+/-5°C. Subsequently, feed for the grout, vitrification, and sulfate vendors will be decontaminated as described below.

3.4 Removing Cesium from the Dissolved Saltcake Solution (Sample 1)

Readily available ion exchange technology will be used to remove Cs from the immobilization test feeds. As directed by CH2M HILL, SuperLig® 644 will be the assumed ion exchange material for removing Cs from the immobilization feed solutions. However, depending on schedule, it might be necessary to apply an alternative technology. The back-up ion exchange material for removing Cs from the feed solution is crystalline silicotitanate (CST). SuperLig® 644 will need to be procured for this effort. The delivery time for the resin is estimated to be 4 to 8 weeks. On the other hand, CST is already available at PNNL and could be deployed immediately. Choice between these two options may be driven by schedule, more than by technical considerations.

The batch K_d for sorption of Cs from the feed solution onto the SuperLig® 644 material will be measured (in duplicate) so that the column to be used can be sized appropriately. The K_d will be measured by mixing a weighed quantity (0.1 g) of SuperLig® 644 with 10 mL of the feed solution. The contact can be performed by mixing with a reciprocal shaker for nominally 24 h. The Cs concentration in the solution before and after contact (following filtration through a 0.2-µm nylon membrane) will be determined and the K_d calculated according to Equation 1:

$$K_d = \frac{C_o - C_1}{C_1} \cdot \frac{V}{m \cdot F} \tag{1}$$

where C_o = initial concentration of cesium in the solution

C_l = final concentration of cesium in the solution

V = volume of solution used in the batch equilibrium experiment

m = mass of ion exchanger used in the batch equilibrium experiment

F = mass of dry ion exchanger/mass of wet ion exchanger (the F-factor)

The bed density (ρ_b) of the SuperLig® 644 material will also be measured so that the column volumes of solution processed before 50% breakthrough occurs can be estimated from the column distribution ratio (λ):

$$\lambda = K_d \rho_b \quad (2)$$

Based on this information, an appropriately sized SuperLig® 644 column will be installed in a hot cell.

The feed solution will be process by passing it through the SuperLig® 644 column. Gamma spectroscopy will be used to verify that the Cs removal is adequate. The criterion for success is a Cs decontamination factor (DF) of 200. The DF is determined by Equation 3:

$$DF = C_{feed}/C_{eluant} \quad (3)$$

3.5 Removing Technetium from the Dissolved Saltcake Solution (Sample 1)

As was the case with Cs, readily available ion exchange technology will be used to remove Tc from the feed solution. Removal of Tc would preferentially be done using SuperLig® 639, but the use of existing stocks of this material might need to be negotiated with the WTP project or additional material would need to be procured. However, as is the case for Cs, elution of the Tc from the column is not of critical concern to the success of this task. Because of this, the use of quaternary ammonium-type anion exchanger could be considered. These materials are readily available. Either way, Tc will be removed by passing the Cs-decontaminated solution through a column containing the appropriate Tc-selective ion exchanger.

The Tc ion exchange column design will be determined in a manner similar to that described above for Cs. For the batch Tc K_d measurements, the solution can be spiked with ^{95m}Tc so that the relative Tc can be rapidly determined by gamma spectroscopy. Spiking with $^{95m}TcO_4^-$ can also be done for the Tc IX column run, so that the pertechnetate DF can be rapidly determined by gamma spectroscopy. The criterion for success is a TcO_4^- decontamination factor (DF) of 10.

3.6 Dissolved Saltcake Solution Concentration Adjustment (Samples 1 and 3)

When provided to the vendors, Samples 1 and 3 should be nominally 5 M Na. It is unlikely that initial dissolution in water will result in a 5 M Na solution, so adjustment of the solution will likely be required. Based on the Na concentration of the liquid phase (determined earlier), the samples will be either diluted with deionized water or evaporated to yield a solution that is 5 M Na. If required, evaporation will be achieved by simply heating the sample at 50 to 60 °C under a stream of nitrogen until the desired volume is reached.

3.7 Sampling and Analysis of Prepared Samples

Portions of the Samples 1 and 3 prepared for the vendors will be taken and subjected to the following analyses: gravimetric suspended solids, ICP-AES for bulk metal ions, IC for anions, TIC/TOC, GEA, AEA (with Pu separation), Tc-99 (ICP-MS), and Sr-90. The samples will be analyzed in duplicate. Table 3.2 lists the analytes to be determined and the minimum reportable quantities for these analytes.

The TRU feed (Sample 2) will be taken and subjected to the following analyses: gravimetric suspended solids, ICP-AES for bulk metal ions, IC for anions, TIC/TOC, GEA, AEA (with Pu separation), Tc-99 (ICP-MS), and Sr-90. The samples will be analyzed in duplicate. Table 3.3 lists the analytes to be determined and the minimum reportable quantities for these analytes.

3.8 Sample Shipment

Personnel at the shipping laboratory will perform activities necessary to meet the regulatory requirements for the shipment of radioactive materials, including but not limited to, performing required analyses, preparing and packaging the samples for shipment, preparing all the required documentation, and assuring that all of the licensing and other regulatory requirements are satisfied. The samples will be loaded and shipped in approved containers such as "hedgehog" sample packages, a USDOT spec 7A type “A” packaging authorized for shipping liquid radioactive materials. Arrangements for transportation of the packages from the shipping laboratory to the destination facility will be established separately.

3.9 Reporting

Reports on the following items will be written. Unless otherwise directed by CH2M HILL, all reports will be cleared for public release and issued as topical reports.

- Sample 1—Sample compositing and feed adjustment
- Sample 1—Filtration, Cs/Tc IX, and analysis (before and after IX)
    - Two reports will be provided. First, a preliminary analysis of the material will be supplied to the vendors shortly after shipment of the decontaminated solution. Later, a more comprehensive report will be issued.
- Sample 2—Sample compositing and analysis
- Sample 3—Sample compositing and analysis

Table 3.2 Liquid Fraction Analyses (Samples 1 and 3)

Analyte	**Target Minimum Reportable Quantity**	**Recommended Analysis Method**
	mg/L	
Al	7.5E+01	ICP-AES
Ba	2.3E+00	
Ca	1.5E+02	
Ce	2.3E+00	
Cd	7.5E+00	
Cr	1.5E+01	
Fe	1.5E+02	
K	7.5E+01	
La	3.5E+01	
Na	7.5E+01	
Ni	3.0E+01	
P	6.0E+02	
Pb	3.0E+02	
U	6.0E+02	
U	7.8E+02	KPA
TOC	1.5E+03 (as C)	Silver catalyze persulfate and furnace oxidation method
TIC	1.5E+02 (as C)	
Hg	1.5E+00	Cold Vapor AA
Cl	3.0E+02	IC
F	1.5E+02	
NO_2	3.0E+03	
NO_3	3.0E+03	
PO_4	2.5E+03 (as P)	
SO_4	2.3E+03 (as S)	
	mCi/L (except as noted)	ICP-MS (AA may be used for Cs determination)
^{127}I	1.5E+00 (mg/L)	
^{129}I	1.8E-05	
^{133}Cs	7.0E-04 (mg/L)	
^{137}Cs	1.5E+00	
^{237}Np	2.7E-02	
^{239}Pu	3.0E-02	
^{240}Pu	1.0E-02	
^{241}Pu / ^{241}Am	8.7E-03(mg/L)	
^{99}Tc	1.5E-03	
^{99}Tc(pertechnetate)	1.5E-03	Separations / Liquid Beta Scintillation without sample oxidation to determine pertechnetate
^{79}Se	9.0E-05	Separations / Liquid Scintillation
^{90}Sr	1.5E-01	
^{238}Pu	1.0E-02	Separations / AEA
$^{239/240}$Pu	3.0E-02	
^{241}Am	3.0E-02	
^{242}Cm	1.5E-01	
$^{243/244}$Cm	1.5E-02	
^{154}Eu	2.0E-03	Extended Counting Time GEA
^{60}Co	2.1E-03	
^{126}Sn	6.0E-03	
^{137}Cs	9.0E+00	
Total Alpha	2.3E-01	Alpha counting
Sum of Alpha (TRU)	N/A	Summation of: Pu-238, Pu-239+Pu-240 (or Pu-239, Pu-240 ICP/MS) and Am-241
Total and Free OH	7.5E+04 mg/L	Titration
Density	**Expected Range** 0.95 –1.5 (gm/mL)	Gravimetric
Dissolved solids	1 to 50 (gm solids/gm supernate)	Gravimetric

Footnote:

[a] MRQs are target values, measurement of chelators and organic phosphates are best effort only, since there is insufficient method data available to set QC parameters.

Table 3.3. Analyses For TRU Sludge (Sample 2)

Analyte	Target Minimum Reportable Quantity	Recommended Analysis Method
	mg/Kg[(a)]	
Al	3.3E+02	ICP-AES
Ba	6.0E+02	
Be	3.0E+00	
Bi	6.0E+03	
Ca	1.8E+02	
Cd	1.1E+01	
Cr	1.2E+02	
Cu	1.8E+01	
Fe	1.4E+02	
K	2.0E+02	
La	6.0E+01	
Li	3.0E+01	
Mg	5.4E+02	
Mn	3.0E+02	
Na	1.5E+02	
Ni	1.6E+02	
Nd	6.0E+02	
P	6.0E+02	
Pb	6.0E+02	
Si	3.0E+03	
Sr	3.0E+02	
Ti	1.5E+02	
U	1.5E+02	
Zr	6.0E+02	
Zn	6.0E+00	
TOC	6.0E+01 (as C)	Silver catalyze persulfate and furnace oxidation method
TIC	3.0E+01 (as C)	
Hg	1.5E+00	Cold Vapor AA
Cl	2.3E+02	IC
F	7.5E+03	
NO_2	4.5E+02	
NO_3	4.5E+02	
PO_4	6.0E+02 (as P)	
SO_4	1.2E+03 (as S)	
	mg/Kg	ICP-MS (KPA can be done for U)
As	3.0E+00	
Ce	6.0E+00	
K	1.5E+03	
U	6.0E+02	
^{99}Tc	6.0E+00	
^{127}I	1.5E+00	
^{133}Cs	7.0E-04	
^{233}U	6.0E+01	
^{235}U	6.0E+00	
^{237}Np	1.8E+00	

Table 3.3 Continued, Analyses For TRU Sludge (Sample 2)

Analyte	Target Minimum Reportable Quantity mCi/Kg	Recommended Analytical Methods
^{129}I	1.8E-05	ICP-MS
^{137}Cs	9.0E-02	
^{151}Sm	TBD	
^{234}U	3.7E-03	
^{236}U	3.8E-04	
^{238}U	2.0E-06	
^{90}Sr	7.0E+01	Separations / Beta Gas Flow Proportional Counter
^{151}Sm	TBD	Beta Counting
^{238}Pu	6.0E-02	Separations / AEA
$^{239/240}$Pu	6.0E+00	
^{242}Pu	3.36E-01	
^{241}Am	1.8E-02	
^{242}Cm	1.2E-02	
$^{243/244}$Cm	1.2E-02	
^{60}Co	1.2E-02	Extended Counting Time GEA
^{125}Sb	6.0E+00	
^{126}Sn	6.0E-02	
^{137}Cs	6.0E-02	
^{154}Eu	6.0E-02	
^{155}Eu	6.0E-02	
^{241}Am	6.0E+00	
Total Alpha	1.0E-03	Alpha Count
Sum of Alpha (TRU)	N/A	Summation of: Pu-238, Pu-239, Pu-240, and Am-241
^{241}Pu	1.2E+00 mCi/Kg	Beta Liquid Scintillation Counting
Physical Property	**Expected Range**	
Wt% Oven Dried Solids	0.1 to 100 wt%	Gravimetric
Density	0.9 to 2.0 gm/ml	Gravimetric
Wt% Undissolved Solids	10 to 50 wt%	Calculation
Wt% Soluble Solids	1 to 50 wt%	Calculation

Footnote:

(a) MRQs are based on dried solids weighs.

4.0 References

DOE/RL-2002-47. 2002. *Performance Management Plan for the Accelerated Cleanup of the Hanford Site,* rev.D, Richland, Washington.

Gasper, KA, KD Boomer, ME Johnson, and GW Reddick, Jr.; and AF Choho, and JS Garfield (Numatec Hanford Corporation). 2002. *Recommendation for Supplemental Technologies for Potential Mission Acceleration*, RPP-11261, Rev. 0, CH2MHILL Hanford Group, Richland, WA.

Herting, DL and DB Bechtold. 2002. *Tank 241-S-112 Saltcake Dissolution Laboratory Test Report*, RPP-10984, Rev. 0, Fluor Hanford, Richland, WA.

Herting, DL. 2001. *Saltcake Dissolution FY 2001 Status Report*, HNF-8849, Rev. 0, Fluor Hanford, Richland, WA.

Josphson, GB, LM Bagaasen, JGH Geeting, PA Gauglitz, GJ Lumetta, and JS Tixier. 2002. *Hanford Mission Acceleration Initiative – Draft Preliminary Testing Recommendations for Supplemental Treatment.* PNNL-14005, Pacific Northwest National Laboratory, Richland, Washington.

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