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Test Plan for Fauske and Associates to Perform Tube Propagation Experiments with Simulated Hanford Tank Wastes

C. D. Carlson

February 1996

**Prepared for the U.S. Department of Energy
under Contract DE-AC06-76RLO 1830**

**Pacific Northwest National Laboratory
Operated for the U.S. Department of Energy
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PNNL-10970

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PACIFIC NORTHWEST NATIONAL LABORATORY

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UNITED STATES DEPARTMENT OF ENERGY

under Contract DE-AC06-76RLO 1830

Printed in the United States of America

Available to DOE and DOE contractors from the
Office of Scientific and Technical Information, P.O. Box 62, Oak Ridge, TN 37831;
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Available to the public from the National Technical Information Service,
U.S. Department of Commerce, 5285 Port Royal Rd., Springfield, VA 22161

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Pacific Northwest National Laboratory
Richland, Washington 99352

Executive Summary

This test plan, prepared at Pacific Northwest National Laboratory for Westinghouse Hanford Company, provides guidance for performing tube propagation experiments on simulated Hanford tank wastes and on actual tank waste samples. Simulant compositions are defined and an experimental logic tree is provided for Fauske and Associates (FAI) to perform the experiments. From this guidance, methods and equipment for small-scale tube propagation experiments to be performed at the Hanford Site on actual tank samples will be developed. Propagation behavior of wastes will directly support the safety analysis (SARR) for the organic tanks. Tube propagation may be the definitive tool for determining the relative reactivity of the wastes contained in the Hanford tanks. FAI have performed tube propagation studies previously on simple two- and three-component surrogate mixtures. The simulant defined in this test plan more closely represents actual tank composition. Data will be used to support preparation of criteria for determining the relative safety of the organic bearing wastes.

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1.0 Introduction

The potential for uncontrolled, condensed-phase chemical reactions involving organic compounds and the nitrate/nitrite-bearing tank wastes have been of concern at the Hanford Site. Historical records have been used to determine the organic species present in the tank wastes, allowing for the thermochemical study of surrogate mixtures (two- and three-component systems) to estimate the hazards associated with these types of reactions (Webb 1995). The next steps in the program are to study simulated tank wastes and actual tank wastes. The study of simulated wastes needs to include not only mixtures of organic compounds that were added to the tanks but also mixtures of the products of radiolytic and thermal degradation as determined by the investigation of simulants (Camaioni et al. 1995) and actual waste (Campbell et al. 1994).

The main objective of this testing program is to provide information concerning the energetics of the reactions of sodium carboxylate complexants with sodium nitrate and nitrite in complex reaction mixtures and the influence of catalysts on the energy requirements, e.g., temperature, for initiating the reactions. This work will be performed in parallel with similar investigations of the actual organic tank wastes. The studies will support the risk-based approach for dealing with the Organic Tanks Safety Issue. To fulfill this objective, reactivity/energetics testing will be performed by Fauske and Associates, Inc., using two flowsheet-based simulated wastes. This test plan will be concerned primarily with tube propagation tests, but some corroboratory tests will be performed with a reactive system screening tool (RSST), differential scanning calorimetry (DSC), thermal gravimetric analysis (TGA)/differential thermal analysis (DTA), and laboratory total organic carbon (TOC) analysis. Because of the limited amount of data collected for this study, no meaningful comparisons among the corroboratory data can be expected. A study using a statistically valid number of data points will be required to provide information on the relative comparability of the various methods for determining the energy content of tank wastes.

2.0 Methods and Rationale

Screening studies of surrogate organic-nitrate/nitrite mixtures using the RSST and tube propagation testing were reported in FY 1995 (Fauske et al. 1995). These studies showed that, given an appropriate fuel-to-oxidant mixture with low water concentration, propagating reactions could be possible. The current tests will show if those reactions are likely in simulants that more closely resemble the wastes in the Hanford tanks. The reactivity/energetics testing of simulated Hanford tank wastes described in this test plan will provide additional information on the potential reaction behavior of the actual wastes present in the tanks. The main testing to be performed will be the tube propagation tests, with the other techniques to be corroboratory tests that will provide some supporting information. Following the simulant testing describe herein, the Tank Data Review Committee and the WHC Tank Waste Remediation Safety Program will select appropriate tanks to be used for the follow-up actual waste testing. It is anticipated that testing with actual wastes will be the final step in the experimental plan for resolving the Organic Tank Safety Issue.

2.1 Simulant Selection

A panel of individuals knowledgeable in tank chemistry and waste compositions was convened to determine the best potential simulant for the reactivity and energetics testing. Candidate recipes included a number of simulants that had been used for other purposes. Among these were a series of Tank 241-SY-101 simulants that had been formulated for use in the Flammable Gas Program (Bryan and Pederson 1994), an average tank composition simulant for calcination/dissolution testing (Delegard et al. 1994), and a simulant based on chemical use and flow sheets used at B-Plant (Scheele et al. 1995).

Since the tanks currently on the Organic Tanks Watch List are all single-shell tanks (SSTs), we determined that using a double-shell tank (Tank 241-SY-101) recipe as the primary basis for the simulant recipe would not serve the best interest of the program; however, we agreed that elements observed in this waste at trace levels should be considered for inclusion in the simulate waste. Upon normalization of the waste types, we found that the average SST composition simulant was very similar to the B-Plant flowsheet simulant except for the nitrate concentration and the nitrate/nitrite ratio, which were both much higher for the average SST composition simulant. The decision was to use a modified version of the B-Plant flow sheet simulant for the majority of the testing, with some testing of the SY-101 simulant to verify the studies with a well-characterized simulant.

The modification to the flow-sheet-based simulant, hereafter referred to as SYM-PAS-95 (PUREX Acidified Sludge), was adding transition metals at concentrations indicated by the average composition in the SSTs (Delegard et al. 1994). In addition, it was determined that, with the composition as presented, the mixture would be stoichiometric with respect to the organic carbon and the nitrate/nitrite mixture at an organic carbon content of about 3.8%. Since this was well below the value for the surrogate mixture that would produce a propagating reaction, it was decided to reduce the sulfate, carbonate, and hydroxide quantities and increase the sodium nitrate and nitrite to give a higher carbon-to-oxidant ratio. To keep the other constituents present and still have a stoichiometric organic-to-oxidant mixture, the maximum organic content that can be added, given the quantities in Appendix A, will be 8.9%. This value was determined using the thermochemical information in

Burger (1995). This maximum percent organic carbon may be slightly different for Recipes 2 (SYM-PAS-95-2) and 3 (SYM-PAS-95-3), depending on the identity and ratio of organics determined by the aging study (see Table 2.1).

The organics added to the inorganic portion of the simulant will represent three different time frames in the aging cycle of the waste (see Table 2.1). The first set of organics will be those added during the processing of wastes at Hanford (e.g., starting materials), namely HEDTA, EDTA, glycolate, and citrate.

The second set of organics will be an estimate of the composition after the initial organic species have aged in a tank for approximately 15 years. The ratios of these components in the second set of organics will be determined by Pacific Northwest National Laboratory staff. These ratios will be determined as a part of the Aging Studies Task from current experiments and new radiolytic studies with the simulants as described in this test plan and will be completed by January 31, 1996. The final set of organics will be those estimated to be present in an advanced stage of aging, oxalate and formate. Each of these mixtures of organics will be added to the base inorganic simulant.

Additional organics are present in the tanks, mainly solvents added during different processing campaigns. It was decided to not include these in the organic mixtures since they will most likely evaporate before or during any reaction event, adding little, if any, energy to the reaction. A full description of the preparation of the simulants will be given in Section 4.0 and the appendixes B, C, D, and E.

When the results of the simulant testing have been obtained, a decision will be made on which actual wastes will be tested to make the corroboration with the surrogate and simulant work. This decision on which tanks will provide the most useful information for the safety program will be made

Table 2.1. Organic Constituents for Energetics Testing^(a)

SYM-PAS-95-1	SYM-PAS-95-2	SYM-PAS-95-3	SYM-PAS-95-4 ^(b)
Initial Feed	Intermediate aging	Advanced aging	Complete aging
HEDTA	EDTA	formate	carbonate
EDTA	NTA	oxalate	
citrate ^(c)	IDA		
glycolate	succinate		
	acetate		
	ED3A		
	ED2As		

(a) All species will be added as the sodium salts.

(b) Added for completeness of information. This simulant will not be tested.

(c) Recipe SYM-PAS-95-1a will be the low citrate formulation and Recipe SYM-PAS-95-1b will be the high citrate formulation.

by following the simulant testing describe herein, the Tank Data Review Committee along with the Safety Program. The actual waste samples will probably be spiked with acetate to ensure the propagation limit is reached and meaningful data are obtained.

2.2 Experimental Variables

To adequately determine the bounding conditions for the reactivity/energetics of simulated Hanford tank wastes, a number of conditions will be varied in this test program. These variables include the nature and quantity of the organic species present (described in Section 3.1), the temperature at which the propagation tests are performed, the concentration of caustic, the presence and quantity of transition metals, and the quantities of aluminum and phosphates present. The final four components are minor constituents within the simulated waste recipes, and the variations will be performed in tests of mixtures with organic content at or just above that which shows propagating behavior, and only RSST measurements will be performed on them.

The main variables in this test plan will be changing the types and concentrations of organic species present in the system. It has been shown that organics will degrade through both radiolytic (Camaioni et al. 1995) and thermal aging (Ashby et al. 1992). Since the energy calculations to determine the relative safety of the tanks are performed on acetate rather than on the degraded organics, the results of the calculations tend to overstate the potential energy release. The types and amounts of organics in the initial simulated waste will be those added during the processing of the waste (see Section 2.1). Two recipes will be created, since citrate was not used in all campaigns and may be present in higher concentrations in some tanks. For the other simulated wastes, aging studies will provide a rate of disappearance/appearance of the various organic species. These estimated rates will allow formulation of simulated wastes that approximate an intermediate aged waste (~15 years after treatment) and an advanced aged waste (~30 years), taking advantage of the reduced reactivity of the wastes.

The temperature at which the tube propagation testing is performed will be varied to relate the data to actual tank conditions of 40 to 60°C. The tube propagation testing performed on the surrogate materials (Fauske et al. 1995) was primarily carried out at room temperature, whereas the temperature in the tanks can be up to 60°C or higher.

Caustic in organic oxidation systems has two potential effects on the heat of reaction of organic-nitrate/nitrite reactions: first, sodium hydroxide is a good heat absorber and will be effective as a diluent to inhibit the reaction; second, hydroxide can be involved in the oxidation of the organics (Burger 1995) and provide a higher heat of reaction than a system without hydroxide. For a complete understanding of the effect, a systematic set of tests including a range from 1.0 to 13 M OH⁻ should be tested, but due to time and budget constraints, only two experiments will be performed. Experiments will be conducted at hydroxide concentrations in the simulated waste of 3.5M OH⁻ and 7.0M OH⁻ (see Table 3.1).

The transition metals are being added because of their potential to catalyze the reactions. This may allow the propagation reaction to proceed at a lower temperature or at a faster rate. Again, a parametric study involving the varying of all of the potential catalytic species should be performed,

but due to time and budget constraints, only two tests will be performed. The concentrations of the transition metals will also be doubled from the initial recipe (see Table 3.1) to determine their effect on the system.

The next variable will be the concentration of the aluminum in the system. Aluminum oxides and hydroxides are poor heat absorbers when compared to other components in the waste and will act as an efficient diluent to inhibit the reaction. This will have the opposite effect of the hydroxide. Again, the concentration of aluminum in the second experiment will be double the initial formulation (in Table 3.1).

Another transition metal that will be varied independently from the rest is manganese dioxide. Manganese dioxide has been shown to be a very efficient catalyst for a number of oxidation reactions and is known to be present in the Hanford waste tanks. The amount of manganese dioxide added will be equal (on a mole basis) to the other transition metals present.

The final chemical component to be varied will be phosphate. Since phosphate is known to catalyze some organic decomposition reactions, the concentration of phosphate in one set of tests will be doubled.

In addition to the variation of the components used in the simulated wastes, some variation of the operating parameters of the techniques will be initiated, namely, the heating rate of the DSC measurements. On a sample that is just at the limit of propagation, the DSC will be performed at 1, 5, 10, and 25°C/minute.

2.3 Tube Propagation Testing

The purpose of performing the tests described in this test plan is to determine if tank wastes are capable of undergoing propagating reactions. To have a propagating reaction, a contact-temperature ignition (CTI) condition must exist, implying that the contact temperature or interface temperature between reacted and unreacted materials must exceed the ignition temperature (for a more complete discussion of the CTI see Fauske et al. [1995]). The ignition temperature of a reaction can be obtained using an RSST (see below), while the combustion temperature is obtained with a tube propagation apparatus described in Fauske (1992). The tube propagation tests are initiated with a 138 Joule source, whereas an actual propagating reaction must use the combustion temperature to initiate the reaction of the next layer. This means that to judge the ability of a mixture to propagate in a mixture, both quantities must be determined. In addition to obtaining the temperature at which propagation occurs, the qualitative result of whether a material will propagate is also obtained.

2.4 Reactive System Screening Tool Testing

As discussed in the previous section, it is vital to obtain the CTI data for a system to determine its reactivity. The RSST will provide information on the ignition temperature of the reaction (Creed and Fauske 1993). In addition to this information, the RSST will provide estimated heat of reaction information on the organic-nitrate/nitrite reaction under study in this test plan.

2.5 Differential Scanning Calorimetry and Total Organic Carbon

Currently, the safety analyses performed on tank samples from the Organic Tanks Watch List include DSC and sometimes TOC analyses as an estimate of the reactivity of the tanks. For this reason, either TOC measurements, DSC measurements, or both are available for a large number of tanks. To relate the results of this testing to actual tank data and for closure of the Safety Issue, these DSC and TOC measurements will be performed on the simulated wastes.

3.0 Simulant Preparation

As stated in Section 2.1, the simulant that will be used is a modified PAS simulant with added transition metals. Table 3.1 shows the components that will be added to make up the inorganic portion of the simulant.

The spreadsheet used to calculate the recipe for the simulant is detailed in Appendix B. The recipe for mixing the inorganic constituents to make the simulated waste is in Appendix C. Various organic species will be added to this simulant to mimic the organic portion of the waste at various stages of aging. Table 2.1 shows the organics that will be added to simulate those in the tanks.

The ratios of the organic constituents for Recipe 1 (SYM-PAS-95-1) have been calculated from the estimated inventories added during operations (Allen 1976). Two ratios (designated Recipe 1a and 1b) will be prepared, one with a low citrate concentration and one with a high citrate

Table 3.1. Modified SIM-PAS-95 Simulant (no organic added)

Species	Formula Weight	Concentration (mole/L)
NaOH	40	3.5500
NaNO ₂	69	1.2650
Fe(NO ₃) ₃ • 9 H ₂ O	404	0.0720
Cr(NO ₃) ₃ • 9 H ₂ O	400	0.0013
Ni(NO ₃) ₂ • 6 H ₂ O	291	0.0026
Mn(NO ₃) ₂	179	0.0019
KNO ₃	101	0.0038
Pd(NO ₃) ₂	230	5.0E-5
RuCl ₄ • 5 H ₂ O	333	5.0E-5
Rh(NO ₃) ₃ • 2 H ₂ O	325	5.0E-5
Ce(NO ₃) ₃ • 6 H ₂ O	434	0.0041
Bi(NO ₃) ₃ • 5 H ₂ O	485	0.0031
Na ₂ SiO ₃ • 9 H ₂ O	284	0.0031
NaNO ₃	85	2.2000
Pb(NO ₃) ₂	331	0.0079
Na ₂ SO ₄	142	0.0081
Na ₃ PO ₄ • 12 H ₂ O	380	0.0081
Al(NO ₃) ₃ • 9 H ₂ O	375	0.0850
NaF	42	0.1036
H ₂ O	18	(as required)

concentration. The molar ratio of the species in Recipe 1a will be 1 : 3.96 : 5.86 : 15.53 for EDTA, HEDTA, citrate, and glycolate, respectively. For recipe 1b, the citrate concentration will be increased two-fold and the ratios will be 1 : 3.96 : 11.72 : 15.53 for EDTA, HEDTA, citrate, and glycolate, respectively. The detailed procedures for adding the organic mixtures to the inorganic base are presented in Appendix D. The ratios for the other recipes will be added as Appendix E.

4.0 Procedure

This procedure will be broken into two major sections. The first will describe an iterative process to determine the go/no-go composition for propagation of each of the simulant recipes; the second will focus on determining the effect of varying some of the inorganic constituents of the simulants.

The limited amount of time and funding available for these experiments may preclude performing all of the testing described in this plan. The tube propagation tests (and corroboratory DSC, RSST, and TOC tests) with the Recipe 1a simulant are the most critical. These results will allow us to compare the different methods currently used to determine the reactivity/energetics of the wastes at the Hanford Site.

4.1 Go/No-Go Criteria Determination

Since there is a limited time within which these experiments can be performed, a complete testing matrix will not be feasible. To obtain the information required, decisions about which tests to perform will be made using the data from previous tests. The logic tree will be as follows:

1. Prepare simulant with required percent organic carbon. The first test will be with 7.5% carbon.
2. On the mixture from step 1, perform tube propagation test.
3. Did the mixture show propagating behavior? If yes, go to step 4a; if not, go to step 4b.
- 4a. Prepare a simulant with percent carbon 1.0% less than in the previous test.
- 5a. On the mixture from step 4a, perform tube propagation test.
- 6a. Did the mixture show propagating behavior? If yes, go to step 4a; if not, go to step 8.
- 4b. Prepare a simulant with percent carbon 1.0% more than in the previous test.
- 5b. On the mixture from step 4b, perform tube propagation test.
- 6b. Did the mixture show propagating behavior? If yes, go to step 8; if not, go to step 7.
7. Is the mixture above stoichiometry, >8.5% carbon for recipes 1a and 1b (the values for recipes 2 and 3 will be determined later). If yes, go to step 9; if not, go to step 4b.
8. Perform a second tube propagation test on both the last sample that showed propagating behavior and the last sample that did not show propagating behavior. Perform duplicate RSST (if sample was dry), DSC, TGA, and TOC tests on both samples.

9. If the sample in the process was dry (no added water), perform RSST, DSC, and TOC analyses on last sample that did not show propagating behavior and TOC only on the last sample that did show propagating behavior.

If the cognizant scientist (H. Fauske) determines that sufficient additional information can be gained from performing Step 9 on wet samples, that will be added to the procedure. Also, if H. Fauske determines that additional mixtures are needed to clarify inconsistent or ambiguous data, the appropriate tests should be performed.

Test instructions will be prepared by FAI using the above description in addition to the appropriate FAI manuals and procedures and added as Appendix F. The decision diagram of this logic tree is shown in Figure 4.1.

The DSC and TGA tests are to be performed in a nitrogen atmosphere. The first two DSC runs will be performed with a heating rates of 1, 5, 10, 25°C/min from room temperature to 700°C. From the results of these tests, the heating rate of all subsequent DSC and TGA runs will be determined. The TOC results will be reported on a dry weight basis.

The tube propagation experiments are described below, listed in order of priority. Following the completion of experiments 1 and 2, a decision will be made by the responsible WHC engineer on which of the remaining tests will be performed and in what order.

- 1) SYM-PAS-95-1a at room temperature, starting with a sample containing a percent carbon of value of 7.5% on a dry weight basis, vacuum dried at 50°C to constant weight.
- 2) SYM-PAS-95-1a at 60°C, starting with the percent carbon observed to propagate in the previous experiment (#1), vacuum dried at 50°C to constant weight.
- 3) SYM-PAS-95-1a at room temperature with the percent carbon observed to propagate in the first experiment (#1), with 5% water added.
- 4) SYM-PAS-95-1a at 60°C, starting with the percent carbon observed to propagate in the previous experiment (#3), with 5% water added.
- 5) SYM-PAS-95-1b at room temperature, starting with the percent carbon observed to propagate in experiment (#1), vacuum dried at 50°C to constant weight.
- 6) SYM-PAS-95-1b at 60°C, starting with the percent carbon observed to propagate in the previous experiment (#5), vacuum dried at 50°C to constant weight.
- 7) SYM-PAS-95-1b at room temperature, starting with the percent carbon observed to propagate in experiment (#5), with 5% water added.

Figure 4.1. Experimental Decision Diagram

- 8) SYM-PAS-95-1b at 60°C, starting with the percent carbon observed to propagate in experiment (#6), with 5% water added.
- 9) SYM-PAS-95-2 at room temperature, starting with the percent carbon observed to propagate in experiment (#1), vacuum dried at 50°C to constant weight.
- 10) SYM-PAS-95-2 at 60°C, starting with the percent carbon observed to propagate in the previous experiment (#9), vacuum dried at 50°C to constant weight.
- 11) SYM-PAS-95-2 at room temperature, starting with the percent carbon observed to propagate in experiment (#9), with 5% water added.
- 12) SYM-PAS-95-2 at 60°C, starting with the percent carbon observed to propagate in experiment (#10), with 5% water added.
- 13) SYM-PAS-95-3 at room temperature, starting with the percent carbon observed to propagate in experiment (#9), vacuum dried at 50°C to constant weight.
- 14) SYM-PAS-95-3 at 60°C, starting with the percent carbon observed to propagate in the previous experiment (#13), vacuum dried at 50°C to constant weight.
- 15) SYM-PAS-95-3 at room temperature, starting with the percent carbon observed to propagate in experiment (#2), with 5% water added.
- 16) SYM-PAS-95-3 at 60°C, starting with the percent carbon observed to propagate in experiment (#13), with 5% water added.
- 17) SY1-SIM-94B (see appendix G for recipe) at room temperature starting with the percent carbon observed to propagate in experiment (#1), vacuum dried at 50°C to constant weight.

If the samples with no moisture do not propagate, the corresponding samples with 5% moisture added need not be run.

4.2 Minor Constituent Effects

One of the initial purposes for performing the testing with simulated waste was to determine the effect of other plausible constituents on the propagation reaction. To determine the effect each of these constituents would require a parametric study in which all of the species of interest were varied. Again, very targeted experiments will be performed in which the amounts of the most important of these constituents will be doubled (with respect to the initial composition in Table 4.1) in an attempt to determine the effect on the propagation behavior of the simulated wastes. Since the catalysts will only affect the activation energy of the reactions, only RSST experiments will be performed on these mixtures, and they will be performed on only one of the organic mixtures, preferably the one that represents 15 or 30 years of aging.

Experiments to be performed:

- 1) Double the caustic concentration.

Sodium hydroxide is a good heat absorber which will decrease adiabatic combustion temperature. Hydroxide can also be involved in the combustion reaction, causing an increase in the heat of the reaction.

- 2) Double the concentrations of metals in the system.

The transition metals are added to this mixture because of their potential to catalyze the reactions. The metals whose concentrations will be doubled are iron, chromium, nickel, manganese, palladium, ruthenium, rhodium, cerium, bismuth, and lead.

- 3) Double the aluminum concentration.

Since aluminate is not as effective a heat absorber as other potential waste constituents, it will not be as effective a diluent as other species such as nitrate and will allow the temperature of the system to increase to higher levels than would other constituents.

- 4) Add manganese (II) oxide as a catalyst.

Manganese is already one of the transition metals in the system, but its availability in the tanks and its high likelihood to catalyze the reaction make it a special case.

- 5) Double the sodium phosphate concentration.

The presence of phosphate has been shown to catalyze organic decomposition reactions.

- 6) During the course of this investigation, other potential catalytic species may be identified. These additional species will be selected for study in consultation with the principal scientist during the course of this study.

All of these mixtures will be analyzed using the RSST and will be performed in duplicate.

5.0 Responsibility

The following is a list of organizations that are responsible for the various aspects of the work described in this test plan:

- Westinghouse Hanford Company - Safety Basis Staff, responsible lead David Turner
- Fauske and Associates (FAI), responsible lead Hans Fauske
- Pacific Northwest National Laboratory - Waste Tank Safety Program Staff, responsible lead Richard Hallen.

Table 5.1. Responsible Organizations for Propagation Testing Program

Responsibility	Lead Organization	Supporting Organizations
Test Plan Preparation	WHC	PNL
Test Instructions	FAI	
Test Plan Review	WHC	FAI, PNL
Simulant Preparation	PNL	FAI
Propagation Testing	FAI	
Actual Waste Selection	WHC ^(a)	
Corroboratory Testing	FAI	WHC, PNL
Data Reduction and Evaluation	WHC	FAI, PNL
Reporting	WHC	FAI, PNL
Quality Assurance	WHC	FAI
(a) Tank Data Review Committee with G. Dukelow (WHC).		

6.0 Data

Data to be collected will include the determination of the go/no-go composition of organic nitrate/nitrite using tube propagation testing, heats of reaction from RSST, and DSC, TOC, and TGA measurements. Table 6.1 shows the types of information that will be collected and suggested methods for reporting those data.

Table 6.1. Data to Be Collected for Each Series of Tests
(e.g., results from SIM-PAS-95-1a tests)

% Organic Carbon (added)	Tube Propagation (Y or N)	Onset Temp. (°C)	DSC Result Exotherms (J/g sample)	TGA Result (% H ₂ O)	TOC Results (dry weight) (%)	RSST Heat of Reaction (J/g sample)
7.5			A	B	C	D
8.5						
8.5						
8.5						
8.5						
<p>A - The average result of the exotherm will be reported, along with the relative percent deviation (RPD).</p> <p>B - The average result of the thermogram will be reported, along with the relative percent deviation (RPD).</p> <p>C - The average result of the TOC analysis will be reported, along with the relative percent deviation (RPD).</p> <p>D - The average result of the exotherm will be reported, along with the relative percent deviation (RPD).</p>						

In addition to reporting this data, the uncertainties in the results will be reported for each category of data.

7.0 Data Control

Data should be collected in a hard-covered laboratory notebook or on data sheets that can be affixed to a notebook. At the beginning of each day of the test activity, initial entries should include, at a minimum, the following information:

- Date
- Test operator
- Current test conditions (temperature, pressure, etc.)
- Planned test activity for the day
- Reference to test procedure/instruction
- Applicable sample identification numbers
- General observations, if any.

8.0 Measurement and Test Equipment

Equipment such as balances, thermocouples, and the like will be calibrated and controlled in accordance with WHC QA requirements. A suggested list of information to be obtained for all of the equipment is as follows: instrument number, associated equipment, location, description of equipment, function, manufacturer, serial number, range, percent error allowed, calibrating agent, calibration frequency, date of last calibration, and due date for next calibration.

9.0 Change Control

Changes affecting the objectives of the testing identified in this test plan shall be reviewed and approved by WHC Safety Basis staff. The significance of the changes will be determined by the WHC project manager or his designated alternate. Major changes will be documented by issuing a revision to this test plan; minor changes will be made by marking issued copies of the current version of this plan. All minor changes shall be signed and dated by the cognizant engineer/scientist (H. Fauske or alternate).

10.0 Quality Assurance

All experimental work will be conducted in accordance with WHC Impact Level III quality assurance requirements. The cognizant WHC Quality Engineer will monitor compliance with applicable QA requirements.

11.0 References

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Appendix A

Determination of Maximum Organic Carbon in Simulated Wastes

Appendix A

Determination of Maximum Organic Carbon in Simulated Wastes

As stated in Section 3.0, the mole ratios of the organics to be used in the first recipe are 1 : 3.96 : 5.86 : 15.53 (1a) and 1 : 3.96 : 11.72 : 15.53 (1b) for EDTA, HEDTA, Citrate, and glycolate, respectively. The mole ratios of oxidant required to fully oxidize each of these organics can be seen in Table A.1 (Burger 1995).

Table A.1. Moles of Oxidant Required to Completely Oxidize the Organic

(moles oxidant/mole organic)	EDTA	HEDTA	citrate	glycolate
nitrate	8	8.8	3.6	1.2
nitrite	13.33	14.67	6.0	2.0

From these data, the amount of organic added to achieve stoichiometry for given concentrations of nitrate and nitrite can be calculated. For the low citrate case:

$$\text{moles of nitrate} = 8x(1) + 8.8x(3.96) + 3.6x(5.86) + 1.2x(15.53)$$

and

$$\text{moles of nitrite} = 13.33x(1) + 14.67x(3.96) + 6.0x(5.86) + 2.0x(15.53)$$

where

$$x = \text{moles of EDTA}$$

Simplifying these expressions gives

$$\text{moles of nitrate} = 82.58x \quad \text{and} \quad \text{mole of nitrite} = 137.64x$$

Therefore

$$(\text{moles of nitrate}/82.58) + (\text{moles of nitrite}/137.64) = \text{moles of EDTA}$$

and

$$\text{moles HEDTA} = (\text{moles EDTA}) \cdot (3.96)$$

$$\text{moles citrate} = (\text{moles EDTA}) \cdot (5.86)$$

$$\text{mole glycolate} = (\text{moles EDTA}) \cdot (15.53)$$

The moles of organic to give stoichiometry in the high citrate case using the same method is:

$$(\text{moles of nitrate}/103.67) + (\text{moles of nitrite}/172.8) = \text{moles of EDTA}$$

and

$$\text{moles HEDTA} = (\text{moles EDTA}) \cdot (3.96)$$

$$\text{moles citrate} = (\text{moles EDTA}) \cdot (11.72)$$

$$\text{mole glycolate} = (\text{moles EDTA}) \cdot (15.53)$$

Appendix B

Calculations for Modified PAS Simulated Waste

Appendix B

Calculations for Modified PAS Simulated Waste

The calculations for PAS94 simulated waste are shown in Table B.1.

Table B.1. Calculations for Modified PAS Simulated Waste

Organic Simulant (PAS94)	Prepared by Clark Carlson			From B-Plant Flow Sheets modified to 7.5% TOC											
					amount	total									
COMPONENT	F. Wt. (g/mol)	M (mole/L)	VOLUME(L)	grams	added	Weight%	wt% Na	wt% Al	wt% PO4	wt% NO2	wt% NO3	wt% F	wt% OH	wt% Cr	
NaOH	40	3.5500	1	142.00	1	11.63	6.6845	0	0	0	0	0	4.9407	0	
NaNO2	69	1.2650	1	87.29	2	7.15	2.3819	0	0	4.7639	0	0	0	0	
Fe(NO3)3 * 9 H2O	404	0.0720	1	29.09	3	2.38	0	0	0	0	1.09637	0	0	0	
Cr(NO3)3 * 9 H2O	400.15	0.0013	1	0.52	4	0.04	0	0	0	0	0.0198	0	0	0.0055	
Ni(NO3)2 * 6 H2O	290.81	0.0026	1	0.76	5	0.06	0	0	0	0	0.02639	0	0	0	
Mn(NO3)2	178.95	0.0019	1	0.34	6	0.03	0	0	0	0	0.01929	0	0	0	
KNO3	101.103	0.0038	1	0.38233	8	0.03	0	0	0	0	0.01919	0	0	0	
Pd(NO3)2	230.41	0.0001	1	0.01153	9	0.00	0.0002	0	0	0	0.00051	0	0	0	
RuCl4*5H2O	332.96	0.0000	1	0.01601	10	0.00	9E-05	0	0.0004	0	0	0	0	0	
Rh(NO3)3*2H2O	324.93	0.0000	1	0.01557	11	0.00	0	0	0.0004	0	0.00073	0	0	0	
Ce(NO3)3*6H2O	434.23	0.0041	1	1.79469	12	0.15	0	0	0	0	0.06294	0	0	0	
Bi(NO3)3 *5H2O	485.07	0.0031	1	1.49287	13	0.12	0	0	0	0	0.04686	0	0	0	
Na2SiO3-9H2O	284.2	0.0031	1	0.88	14	0.07	0.0117	0	0	0	0	0	0	0	
NaNO3	84.99	2.2000	1	186.98	15	15.31	4.1425	0	0	0	11.1667	0	0	0	
Pb(NO3)2	331.23	0.0079	1	2.62	16	0.21	0	0	0	0	0.0401	0	0	0	
Na2SO4	142.04	0.0081	1	1.15	17	0.09	0.0305	0	0	0	0	0	0	0	
Na3PO4 * 12 H2O	380.13	0.0081	1	3.08	18	0.25	0.0458	0	0.063	0	0	0	0	0	
Al(NO3)3* 9 H2O	375.13	0.0850	1	31.89	19	2.61	0	0.1879	0	0	1.29433	0	0	0	
NaF	41.99	0.1036	1	4.35	20	0.36	0.1951	0	0	0	0	0.16	0	0	
H2O	18	40.3800	1	726.84	21	59.50	0	0	0	0	0	0	0	0	
TOTAL			1	1221.48		100.00	13.492	0.1879	0.0637	4.7639	13.7933	0.16	4.9407	0.0055	
TOTAL WEIGHT	1221.4837	g	DENSITY	1.22											

Table B.1 (contd)

Organic Simulant (PAS94)	Prepared by Clark Carlson				From B-Plant Flow Sheets modified to 7.5% TOC									
COMPONENT	wt% Fe	wt% Ni	wt% SO ₄	wt% Ca	wt% H ₂ O	Wt% Cl	wt% Pb	wt% Pd	wt% Ru	wt% Rh	wt% Ce	wt% Bi	wt% Mn	Total wt%
NaOH	0	0	0	0	0	0	0	0	0	0	0	0	0	11.63
NaNO ₂	0	0	0	0	0	0	0	0	0	0	0	0	0	7.15
Fe(NO ₃) ₃ * 9 H ₂ O	0.3289	0	0	0	0.9549	0	0	0	0	0	0	0	0	2.38
Cr(NO ₃) ₃ * 9 H ₂ O	0	0	0	0	0.0172	0	0	0	0	0	0	0	0	0.04
Ni(NO ₃) ₂ * 6 H ₂ O	0	0.012	0	0	0.023	0	0	0	0	0	0	0	0	0.06
Mn(NO ₃) ₂	0	0	0	0	0	0	0	0	0	0	0	0	0.0085	0.03
KNO ₃	0	0	0	0	0.0111	0	0	0	0	0	0	0	0	0.03
Pd(NO ₃) ₂	0	0	0	0	0.0001	0	0	0.00044	0	0	0	0	0	0.00
RuCl ₄ *5H ₂ O	0	0	0	0	0.0004	0.00056	0	0	0.0004	0	0	0	0	0.00
Rh(NO ₃) ₃ *2H ₂ O	0	0	0	0	0.0001	0	0	0	0	0.0004	0	0	0	0.00
Ce(NO ₃) ₃ *6H ₂ O	0	0	0	0	0.0365	0	0	0	0	0	0.0474	0	0	0.15
Bi(NO ₃) ₃ *5H ₂ O	0	0	0	0.0101	0.0227	0	0	0	0	0	0	0.05265	0	0.13
Na ₂ SiO ₃ -9H ₂ O	0	0	0	0	0.0411	0	0	0	0	0	0	0	0	0.05
NaNO ₃	0	0	0	0	0	0	0	0	0	0	0	0	0	15.31
Pb(NO ₃) ₂	0	0	0	0	0	0	0	0	0	0	0	0	0	0.04
Na ₂ SO ₄	0	0	0.0637	0	0	0	0	0	0	0	0	0	0	0.09
Na ₃ PO ₄ * 12 H ₂ O	0	0	0	0	0.1432	0	0	0	0	0	0	0	0	0.25
Al(NO ₃) ₃ * 9 H ₂ O	0	0	0	0	1.1273	0	0	0	0	0	0	0	0	2.61
NaF	0	0	0	0	0	0	0	0	0	0	0	0	0	0.36
H ₂ O	0	0	0	0	59.505	0	0	0	0	0	0	0	0	59.50
TOTAL	0.3289	0.012	0.0637	0.0101	61.882	0.00056	0	0.00044	0.0004	0.0004	0.0474	0.05265	0.0085	99.82
TOTAL WEIGHT														

Appendix C

Preliminary Recipe for Preparing Modified PAS Simulated Waste

Appendix C

Preliminary Recipe for Preparing Modified PAS Simulated Waste

(PRELIMINARY; may be modified when simulated waste preparation is performed by PNL)

- 1) Obtain chemicals listed in Appendix B. Make sure all chemical are ACS Reagent grade.
- 2) To make a one (1) liter batch, add 500 mL of deionized water to a 1.5 L (or larger) beaker with an appropriate stirrer.
- 3) Add the sodium hydroxide, sodium nitrite, and sodium nitrate to the water and stir until dissolved.
- 4) Place all metal nitrates into a beaker and dissolve in 20 mL of water.
- 5) Add metal nitrates to large beaker and stir.
- 6) Add sulfate, phosphate and halides to mixture and stir until dissolved.
- 7) Add remaining water to bring the solution up to 1 liter.
- 8) Place in a 50°C vacuum oven and dry to a constant weight.
- 9) After drying, grind and homogenize sample to less than 100 mesh.

Appendix D

Procedure for Addition of Organic to Modified PAS Simulated Waste

Appendix D

Procedure for Addition of Organic to Modified PAS Simulated Waste

(PRELIMINARY; may be modified during preparation of simulated wastes)

To prepare the mixtures of organic salts to be used in the preparation of simulated wastes, the sodium salts will be mixed together as outlined in Table D.1. The mixtures will be prepared dry and ground to less than 50 mesh.

- 1) Weigh out 20 grams of modified PAS simulated waste into a 150 mL beaker with a stirring apparatus (magnetic stir bar or equivalent).
- 2) Add 100 mL of deionized water followed by the appropriate amount of mixed organic solids (see Table D.2) and stir for 30 minutes.
- 3) Stir and heat solution ($<50^{\circ}\text{C}$) until free liquid is removed.
- 4) Place mixture in a 50°C vacuum oven and dry to constant weight.
- 5) Homogenize and grind to less than 100 mesh.

Table D.1. Quantities and Identification to Prepare Mixtures of Organic Salts

Recipe 1a		Recipe 1b		Recipe 2		Recipe 3	
Species	Mass	Species	Mass	Species	Mass	Species	Mass
Na_3HEDTA	29.34 g	Na_3HEDTA	21.96 g	EDTA	TBD	formate	TBD
Na_4EDTA	7.41 g	Na_4EDTA	5.55 g	NTA	TBD	oxalate	TBD
$\text{Na}_3\text{citrate}^{(a)}$	33.59 g	$\text{Na}_3\text{citrate}^{(a)}$	50.28 g	IDA	TBD		
Na-glycolate	29.66 g	Na-glycolate	22.21 g	succinate	TBD		
				acetate	TBD		
				ED2As	TBD		

(a) Citrate is used as the sodium monohydrate salt.

Table D.2. Mass of Organic Salt Added to 20 Grams of Simulated Waste Mixture

Target % Carbon	Recipe 1a	Recipe 1b	Recipe 2	Recipe 3
8.5	9.147	9.481		
7.5	7.659	7.924		
6.5	6.315	6.523		
5.5	5.096	5.256		
4.5	3.985	4.104		
3.5	2.968	3.053		

Appendix E

Organic Species and Ratios from Aging Studies

Appendix E

Organic Species and Ratios from Aging Studies

The material for this appendix will be added as it is developed.

Appendix F

Test Instructions

Appendix F

Test Instructions

To be completed by FAI.

Appendix G

Calculations for SY1-SIM-94B Simulant

Appendix G

Calculations for SY1-SIM-94B Simulant

The material for this appendix will be added as it is developed.

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