Surrogate Treatment Plan

<u>Modified TCLP amount:</u>

Surrogate (4500N): (10 g for extraction + 5 g for pH check) x 2 for duplicate = 30 g sample
Hot (2026): 10 g including duplicate according to Keller? As low as 2 g!

Surrogate & W23 TCLP conducted in triplicate for each phase => 90 g surrogate solids & 6 g hot solids minimum for each "phase" or 180 g surrogate solids equally split between phases & 12 g hot solids equally split between phases.
May not have the resources to do the MVST samples in triplicate (6 samples x 2 "phases" x 3 TCLPs each = 36 TCLPs), so these may be single TCLP for each phase of 6 separate MVST tank samples.

<u>Test "Quick & Dirty" surrogate (reagent grade chemicals + water):</u> We will prepare approximately 200 g (dry weight) of the simple W23 waste sludge surrogate made from a mix of reagent grade chemicals and water (one of two W23 surrogates listed in the spreadsheets by Roger Spence; see 'w23 surrogate design.123' or 'w23 surrogate design.wk4'). The test procedure as outlined below will be followed to stabilize this surrogate; no long term testing will be done with this surrogate.

We plan to prepare 2 kg of the more representative MVST surrogate made by high pH precipitation of the metals from a nitrate solution. This amount should be ample for both initial and long term stability tests.

Laboratory Procedure Emulating FWENC Process (Backbone of Surrogate Work)

1. Prepare Surrogate (formulation given to FW in previous correspondence from R. Spence)
2. Mix 1 mass of raw form surrogate with 3.8 masses of process water for 30 minutes aggressively.
3. Settle for at least 12 hours and record any subjective observations.
4. The top layer above apparent solids level will be decanted. This is to within practical limits--some supernate may remain with solids.
5. Measure the mass of each "phase" – the decanted supernate and settled solids fraction – and compare to the initial mass (starting mass of surrogate sludge and process water).
6. Cover or seal each phase while not in use, to retard evaporative losses before processing.

With Decanted Supernate:

1. Measure the loss on drying (LOD) at 110°C of a small sub-sample of the decanted supernate and submit a sub-sample for measurement of total concentration of the Hg, Pb, Cd, and Cr (the only RCRA metals included in the surrogate) in the supernate after washing.
2. Calculate the target mass range to concentrate all of the decanted supernate to approximately 45-50% TS (total solids) and evaporate to this mass range using vacuum evaporation (~20 "Hg at 180 °F). If the mass falls below the target range, but the sample still contains a liquid layer and the mass is within "reasonable" range of the target range, add enough water to bring sample back within mass range. If the sample has dried (no liquid), re-dissolve the dried sample and re-evaporate to correct mass. DO NOT CONCENTRATE THE SUPERNATE UNATTENDED (E.G., OVERNIGHT) TO DECREASE THE CHANCES OF OVER-EVAPORATING.
3. Calculate if the sample contains enough of the RCRA metals to theoretically fail TCLP, if dry. (The assumption is that the RCRA metals in this phase are dissolved and will completely extract during TCLP after drying, unless stabilized. TCLP is not meaningful on a liquid sample, only total concentration, which can be calculated from the total concentration from Step 1, until solids begin precipitating. However, only the final dried product and its TCLP performance is of real interest.)
4. Estimate the amount of concentrated supernate needed to give enough solids for TCLP testing after processing and use it as the baseline sample size for the remaining process steps. If this quantity exceeds the total amount of concentrated supernate, then process all.
5. If the theoretical calculation in Step 3 indicates no TCLP failure, dry the concentrated sample to a constant weight under a partial vacuum (~20 "Hg) at 180 °F. Measure the LOD at 110°C on a small sub-sample of the dried product. Measure the TCLP performance of this dried sample. If it passes, stop processing the supernate at this point and repeat Steps 4 and 5 two more times (i.e.,

dry and test per TCLP in triplicate), if there is enough concentrated supernate. If the calculation indicates TCLP failure or drying without stabilizes results in TCLP failure, then proceed to the next step and stabilize before drying.

6. Treat sample size estimated in Step 4 with Thio -Decant-1 (optimum formula)
    a. Add at 0.12 X original concentrated sample mass
    b. Mix for at least 15 minutes
    c. Allow to react for at least another hour
    d. Add ET soil polymer at 0.01 X original concentrate sample mass
    e. Mix for at least 15 minutes
    f. Allow to sit/react for at least 6 hours
    g. Dry under a partial vacuum (~20 "Hg) at 180 ^{o}F to a constant weight. Measure the LOD at 110°C on a small sub-sample of the dried product. Measure the TCLP performance of this dried sample. If it passes, then stop processing at this point, and repeat Step 6 two more times (i.e., conduct stabilization, drying, and TCLP in triplicate), quantity permitting.
7. If TCLP results from Step 6 above do not meet acceptance criteria, another sample (see Step 4 for amount) will be treated with Thio-Decant-2 (alternative formula)
    a. Add at 0.2 X original concentrated sample mass
    b. Mix for at least 15 minutes
    c. Allow to react for at least another hour
    d. Add ET soil polymer at 0.01 X original concentrate sample mass
    e. Mix for at least 15 minutes
    f. Allow to sit/react for at least 6 hours
    g. Dry under a partial vacuum (~20 "Hg) at 180 oF to a constant weight. Measure the LOD at 110°C on a small sub-sample of the dried product. Measure the TCLP performance of this dried samp le. If it passes, then stop processing at this point, and repeat Step 7 two more times (i.e., conduct stabilization, drying, and TCLP in triplicate), quantity permitting.
8. The step above – Step 5, 6, or 7 – that results in a blend that meets acceptance criteria will be used to process remaining supernate material, which will be stored for long term stabilization testing.
9. If none of the treatment options meet the acceptance criteria, the concentrated supernate will be stored until alternative treatment plans are made.

With Settled Solids Fraction:

1. Measure the loss on drying (LOD) at 110°C of a small sub-sample of the settled solids fraction and submit 3 sub-samples for TCLP testing.
2. Calculate the amount of wet sludge required to give enough dried sludge for TCLP testing and use it as the baseline sample size for the remaining process steps
3. If the wet sludge passes TCLP, dry it to a constant weight under a partial vacuum (~20 "Hg) at 180 ^{o}F. Measure the LOD at 110°C on a small sub-sample of the dried product. Measure the TCLP performance of this dried sample. If it passes, stop processing the sludge at this point, repeat Steps 2 and 3 two more times (i.e., dry and test per TCLP in triplicate), and process the remainder of the sludge in a similar manner. If the sludge fails TCLP, wet or dry, then proceed to the next step and stabilize before drying.
4. Treat with Th-Sludge-1 (optimum formula)
    a. Add at 0.1 X original settled sludge mass
    b. Mix for at least 15 minutes
    c. Allow to react for at least another hour
    d. Add ET soil polymer at 0.01 X original settled sludge mass
    e. Mix for at least 15 minutes
    f. Allow to sit/react for at least 6 hours
    g. Dry under a partial vacuum (~20 "Hg) at 180 ^{o}F to a constant weight. Measure the LOD at 110°C on a small sub-sample of the dried product. Measure the TCLP performance of this dried sample. If it passes, then stop processing at this point, and repeat Step 4 two

more times (i.e., conduct stabilization, drying, and TCLP in triplicate), quantity permitting.

5. If Step 4 above results in a blend that meets acceptance criteria, then the remaining settled solids will be treated with the same method.
6. If Step 4 does not result in a blend that meets acceptance criteria, then a separate sample will be treated with Th-Sludge-2 (alternative formula)
   a. Add at 0.2 X original settled sludge mass
   b. Mix for at least 15 minutes
   c. Allow to react for at least another hour
   d. Add ET soil polymer at 0.01 X original settled sludge mass
   e. Mix for at least 15 minutes
   f. Allow to sit/react for at least 6 hours
   g. Dry under a partial vacuum (~20 "Hg) at 180 ^{o}F to a constant weight. Measure the LOD at 110°C on a small sub-sample of the dried product. Measure the TCLP performance of this dried sample. If it passes, then stop processing at this point, and repeat Step 6 two more times (i.e., conduct stabilization, drying, and TCLP in triplicate), quantity permitting.
7. If Step 6 above results in a blend that meets acceptance criteria, then the remaining settled solids will be treated with the same method.
8. If none of the process steps - Steps 3, 4, or 6 - produce an acceptable blend, remaining settled solids will be stored until further treatment plans are made.

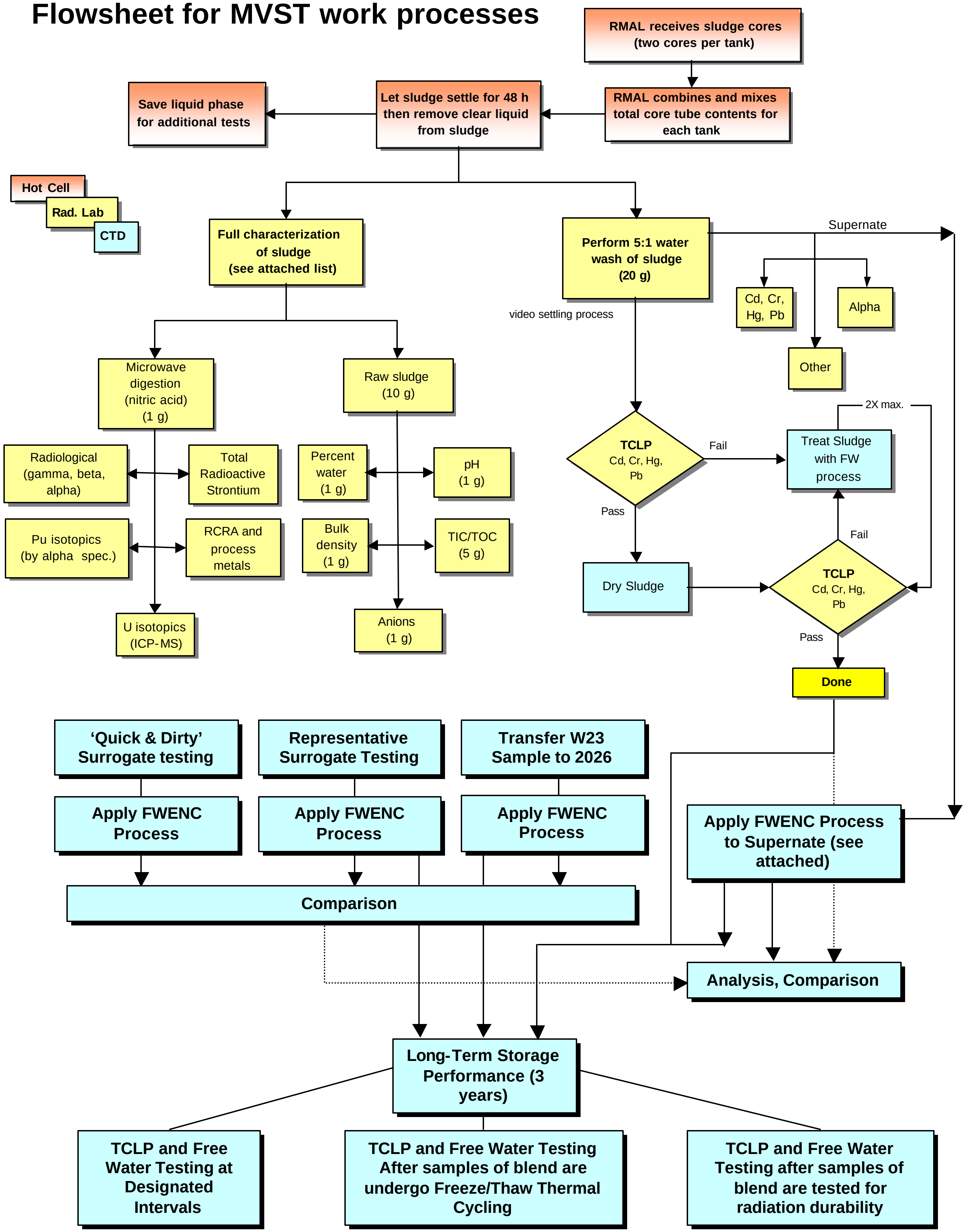
Storage Performance

Assuming that a stabilized blend is produced during initial testing, we will use the remaining settled solids (and supernate material if adequate) for tests of storage performance over a 3 year period. Exact details of how these tests will proceed will be dependent upon how much material remains after initial preparation.

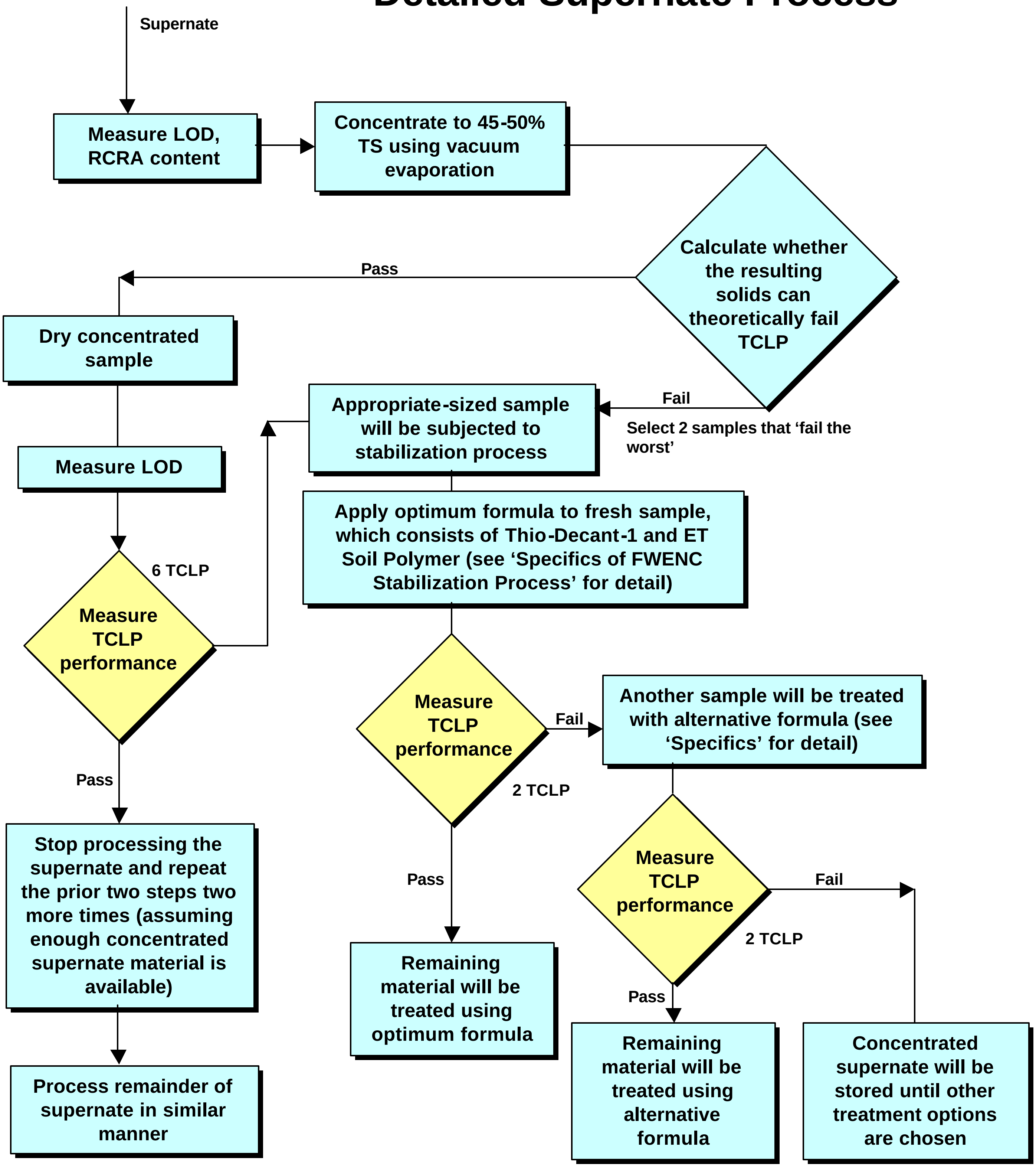
If equipment and facilities are available and operational, we plan to perform the following three types of testing:

1. TCLP and free water testing at designated intervals over the three-year period under standard storage conditions.
2. TCLP and free water testing after samples of blend have been subjected to Freeze/Thaw thermal cycling.
3. TCLP and free water testing after samples of blend have been tested for radiation durability (may use the standard NRC irradiation of 10^8 Rads).

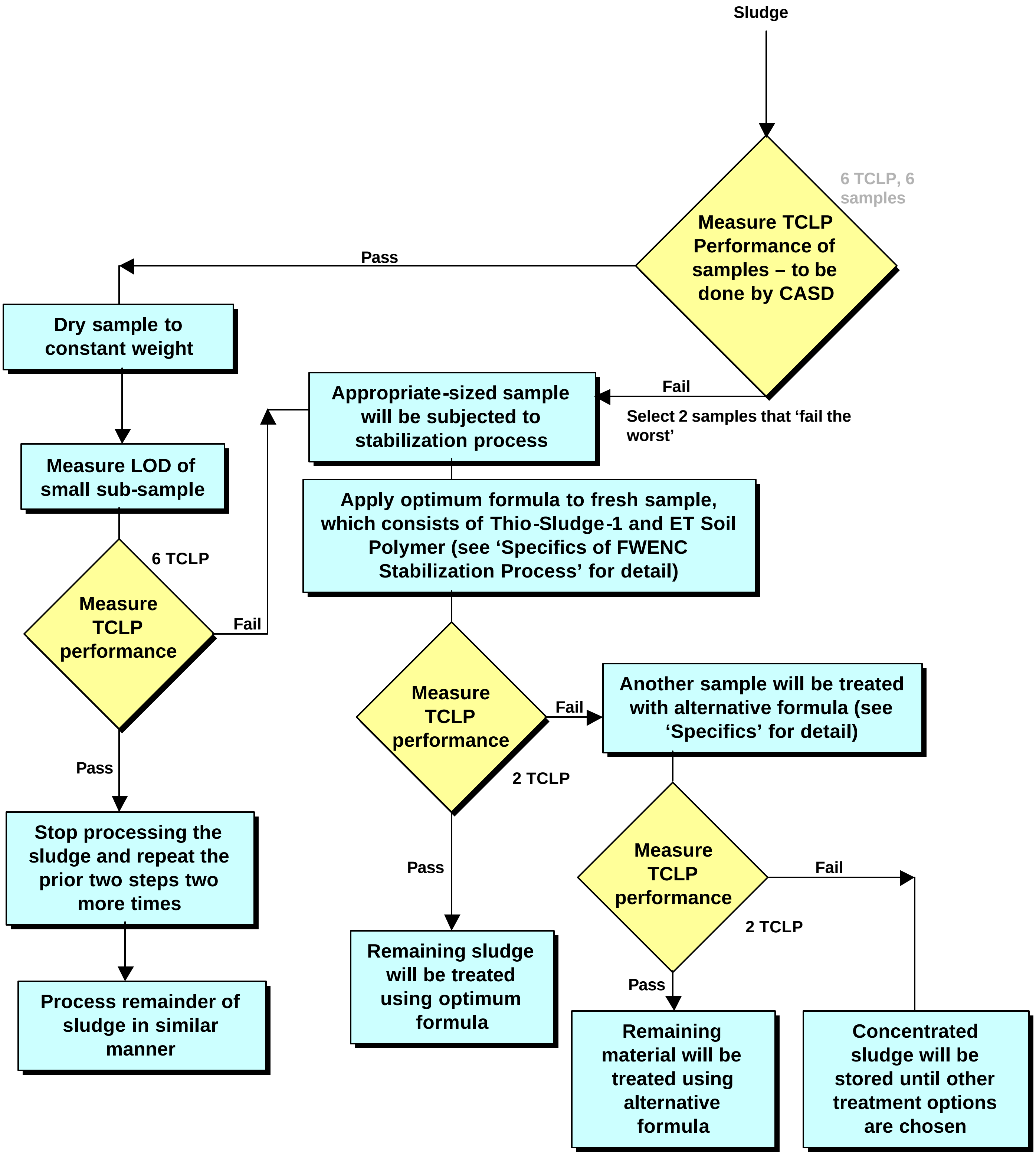
Flowsheet for MVST work processes



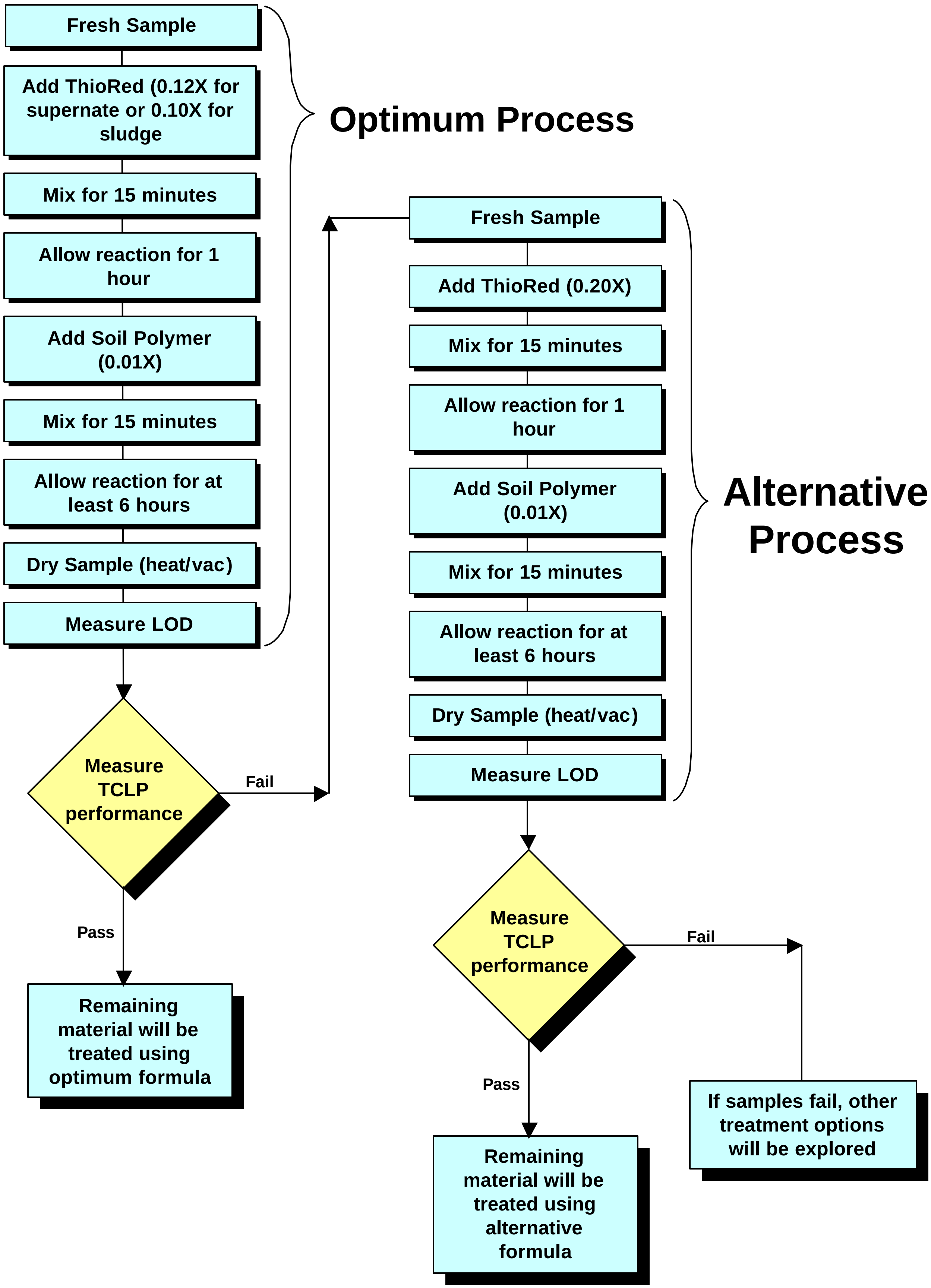
Detailed Supernate Process



Detailed Sludge FWENC Treatment



SPECIFICS OF FWENC STABILZATION PROCESS



05/24/2000 Barton/Spence OR0-0-WT-31, 3TKH – Milestone A3 – ORNL Immobilization

Long Term Testing Plan of FWENC-Stabilized Waste Blends

Background

One objective of TTP OR0-0-WT-31, 3TKH, is to evaluate the performance of the Foster Wheeler Stabilization Process in terms of TCLP performance and free water affinity of surrogate and actual waste blends as a function of storage time, environmental condition, and radiation durability. This document contains a test plan spanning three years for evaluation of performance sustainability of the treated blends to determine suitability of the proposed process.

If equipment and facilities are available and operational, we plan to perform the following three types of testing on treated surrogate and sludges:

1. TCLP and free water testing at designated intervals over the three-year period under storage conditions that simulate East Tennessee environment/ambient.
2. TCLP and free water testing after samples of blend have been subjected to freeze/thaw thermal cycling.
3. TCLP and free water testing after samples of blend have been tested for radiation durability.

TCLP and Free Water Testing at Designated Intervals

We will store FWENC-treated surrogate and FWENC-treated sludge samples (W23 and MVST), and FWENC-treated supernate samples (W23 and MVST) for a period of three years. We will pull approximately 50 dry g of each mixture at 6 month intervals for a period of 3 years and submit these samples for TCLP and free water testing (in triplicate). Depending on budget considerations, we may elect to do only single TCLP on MVST samples. This will require a supply of 300 dry gram of each mixture. It is likely that we will not have enough solids to complete all of the tests on the supernate samples since these are expected to be small by virtue of the process that generates them. We will modify the test plan accordingly to space testing of these over broader time ranges.

The TCLP procedure to be followed will require approximately 10 dry g of the blend for each single analysis. Free water testing will be used to determine how much moisture is absorbed by the blends. Hydration will be monitored using standard loss on drying techniques (drying until constant weight at 110 degrees C). Samples will be checked for any free standing liquid first, which should be < 0.5% volume of the waste. If necessary, a paint filter test or other suitable test will be employed to measure the free standing volume.

This part of the plan will require approximately 18 TCLP samples for each waste blend (3 every six months for three years), with potentially 10 waste blends (surrogate, W23, 3 MVST batches—both supernate and sludge) being examined. Thus a maximum possible number of 180 samples will be analyzed.

Conditions of Storage. To simulate storage conditions that would be expected of a treated waste form in east Tennessee, we will store surrogate samples in an artificially humid (not air conditioned) atmosphere representative of changing ambient. An appropriate storage unit suitable for these samples has been identified. Although highly radioactive samples, W23 and MVST, must be kept in hot cells or vaults, we will store these samples in two sets—one in which humidity is not controlled and another in which an artificially constant and high humidity (75% relative or greater) is generated. These tests will simulate stability upon environmental exposure. Humidity levels will be controlled by use of saturated salt solutions in close proximity to samples. Note: for East Tennessee, relative humidities vary from about 35 to 75% over the course of the year and normal weather, with some short-lived outliers associated with extreme weather conditions.

Radiation Testing

In accordance with the requirements of 10 CFR 61.56(b)(1), irradiation testing of solidified waste forms should be conducted on specimens by exposure to a minimum dose of 10^8 Rads. This dose of radiation is approximately equivalent to the dose that would be acquired by a waste form over a 300-year period, if the waste form were loaded to a Cesium-137 or Strontium-90 concentration of 10 Ci/cu. Ft. This is the recommended maximum activity level for waste forms that contain organic media. In this particular case, the FWENC process calls for use of an organic stabilizing agent that could potentially break down under strong dosage. A minimum of three specimens will be tested for each waste formulation. Instead of the 10^8 Rad dosage recommended, we may elect to first calculate and then use the expected dose based on radiation levels measured for the MVST samples that are collected (data not yet available for calculation). Although less conservative, this approach is likely to be more representative of true storage conditions.

A cobalt source, located in Bldg 4501, will be used to conduct this irradiation on approximately 30 dry grams of each of the 10 blends (if enough material is present).

Following irradiation, these samples will be submitted for triplicate (depending on budget) TCLP analysis. Approximately 30 TCLP analyses will be needed.

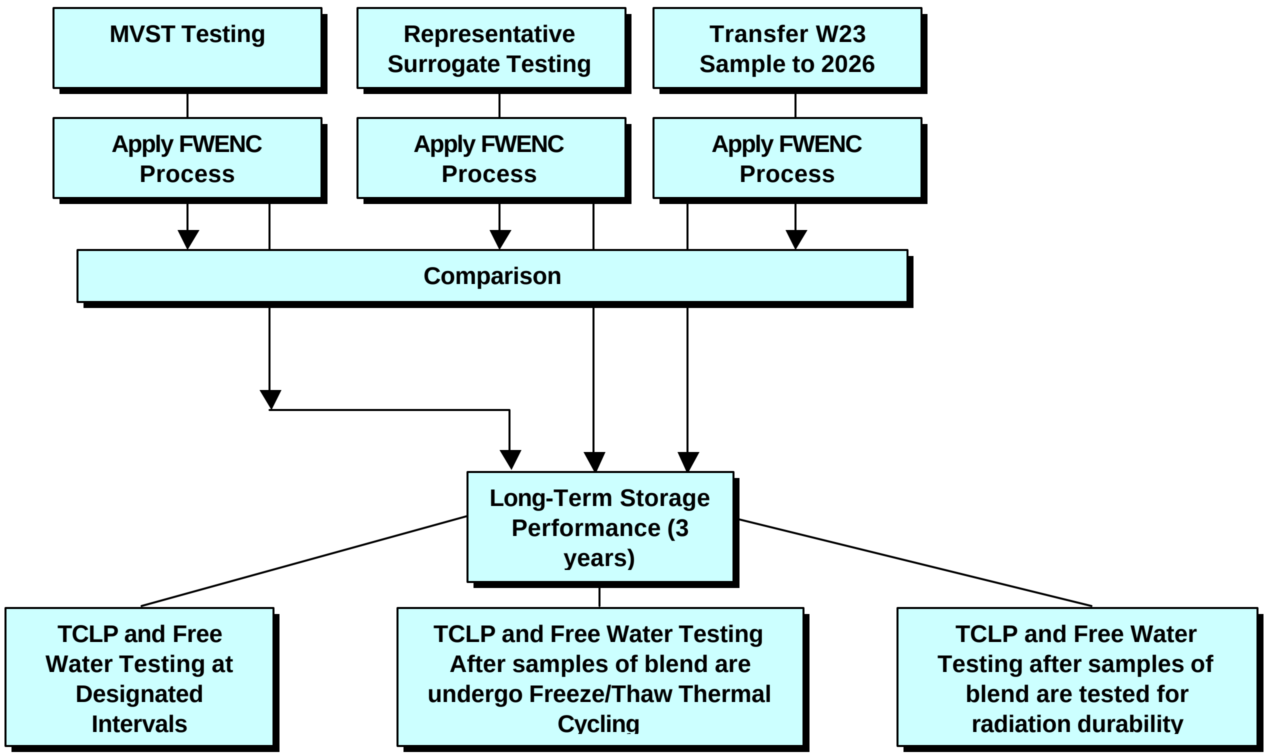
Thermal Degradation Testing

10 CFR 61.56 recommends that internal factors such as temperature and thermal effects be assessed to assure that a waste form retain stability. Thermal cycling of the MVST waste form is most likely to occur during the storage and transport phase of the waste form's performance 'life'. Experience has shown that thermal cycling tests have served well in distinguishing between 'strong' and 'weak' solidified waste forms. By cycling between the maximum and minimum temperatures called for in the NRC's standardized thermal stability test for solid wastes, the extent of any degradation that might occur can be measured. Such degradation is a function of various factors, including the morphology of the microconstituents, the bond strength between the materials present, and the amount and types of cementitious additives present. We borrow this test primarily to explore the potential for free water appearance and will test for any sign of TCLP change. This

test will be conducted under both high humidity (75% or greater) and low humidity conditions (air conditioned ambient).

Specimens will be placed in a thermal cycling test chamber and a series of 30 thermal cycles will be conducted. The specimens will be allowed to come to thermal equilibrium at both the high (60 degrees C) and low (-40 degrees C) temperature limits. A minimum of the three specimens for each waste formulation will be subjected to the thermal cycling tests.

Following irradiation, these samples will be submitted for triplicate TCLP analysis. Approximately 30 TCLP analyses will be needed.



OAK RIDGE NATIONAL LABORATORY
MANAGED BY UT-BATTELLE FOR THE DEPARTMENT OF ENERGY

Fax: (865) 574-6442
bartonjw@ornl.gov

June 29, 2000

Ms. Jacquie Noble-Dial
Field Office Site Representative
U.S. DOE, Oak Ridge Operations Office
P.O. Box 2001, MS-EW-92
Oak Ridge, Tennessee 37830-8620

Dear Ms. Noble-Dial:

This letter is written to formally announce that we have completed HQ-Level Milestone A3 for TTP OR0-0-WT-31, 3TKH, Technical Response 99019, ORNL Immobilization. This milestone was entitled, "Complete testing of surrogate sludge and initiate tests on actual sludge sample." We will issue a report to you at the end of July detailing the experimental results from this milestone.

Please let me know if any other individuals who are not listed below should receive this document.

For additional information, please contact Roger Spence at 865-574-6782.

Sincerely,

JWBarton

J. W. Barton
Staff Engineer, Chemical Technology Division
ORNL

Enclosure

cc: J. Harbour (SRS)
B. Holtzscheiter (SRS)
L. Klatt (ORNL)
R. Spence (ORNL)

ORNL CERS/TFA/005

ORNL IMMOBILIZATION: Surrogate Results

OR00WT31, 3TKH

John Barton
Roger Spence

July 31, 2000

SUMMARY: This document contains results from studies conducted for verification of a FWENC-proposed stabilization process for treating tank wastes. Two surrogate tank wastes were used in this study. Without any treatment, both surrogates failed TCLP EPA limits on three RCRA metals. Using the 'Optimum' formulation provided by FWENC, both rinsed tank sludge surrogates were stabilized and passed TCLP. The supernate/wash/rinse from one surrogate passed TCLP after 'Optimum' treatment; the supernate/wash/rinse from a more representative surrogate failed TCLP (in mercury) after both an 'Optimum' and 'Alternative' treatment. Surrogates failed to reach Universal Treatment Standard limits after both 'Optimum' and 'Alternative' treatments. Based on initial characterization of MVST tank sludges, it is likely that the FWENC 'Optimum' treatment will stabilize tank contents to TCLP EPA limits. It may be possible to reach UTS limits as well, particularly on the rinsed sludges.

Introduction

This report details results from stabilization studies of two different surrogate tank wastes. The stabilization process used was developed by Foster Wheeler Environmental Corporation (FWENC) and basically combines techniques of sluicing, dehydration, and stabilizer addition steps to achieve a final solid waste product that no longer displays the characteristic of toxicity as outlined in 40 CFR 261.24.

Toxicity of a waste is measured as the potential for the toxic constituents in the waste to leach out and contaminate groundwater at levels of concern to human health and the environment. To determine if a waste exhibits the toxicity characteristic, constituents are extracted in a procedure that simulates leaching action in municipal landfills (Toxic Characteristic Leaching Procedure [TCLP], EPA Test Method 1311). Details regarding the Toxicity Characteristic as defined by EPA can be found at http://www.epa.gov/docs/epacfr40/chapt-I.info/subch-I/40P0261.pdf; details regarding the TCLP method can be found at http://oecdwsrv.oecd.ornl.gov/landerin/epb006.html

Methods

The FWENC process is diagrammed in **Figures 1**, **2**, and **3**, which can be found at the end of this document. Tank surrogates are first washed with 5 parts water to 1 part wet surrogate sludge and allowed to settle. This generates two fractions, referred to as 'sludge' (settled solids) and 'supernate' (decanted liquid) in this report. Samples from each fraction are tested to determine whether the fraction displays, or will display, the toxicity characteristic in its final dehydrated form. If either fraction fails to pass, then samples from that fraction are treated using an 'optimum' formulation of chemical additives, and then retested for toxicity characteristics. If this treatment fails, an 'alternative' formulation is used to treat another set of samples, followed by a toxicity analysis.

Two surrogates were used in this study. One is referred to as QnD (Quick and Dirty) surrogate, while the other is called 'W23S', a highly representative surrogate for W23 Tank waste. The QnD surrogate formulation had been used in prior treatability studies of W23 tank wastes (see TM___). This surrogate was prepared by simple mixing RCRA, process, and radionuclide metals together to generate a rough simulation of the composition of tank wastes. A more representative surrogate, W23S, was prepared by mixing RCRA, process, and radionuclide metal compounds, mainly nitrates, together followed by a sodium hydroxide precipitation of the component metals. A volume of water 1.5 times larger than the volume of the precipitated mixture was then used to remove soluble salts from the precipitate. The resulting filter cake and liquid filtrate were re-analyzed for both cation and anion components. The solids were then amended with the necessary amounts of requisite chemicals, including water, to bring the final composition to within 2% (weight fraction) of actual W23 tank waste composition in more than 20 major constituents (both anion and cation). This surrogate was designed specifically for the actual W23 sludge sample to be used in hot testing. **Appendices A** and **B** contain the ionic constituents and their concentrations for both surrogates and the W23 sludge sample. Note that although we are defining the sludge wash as 'supernate', no actual tank supernates, surrogate tank supernates, or actual tank samples were tested in this phase of the work. During FWENC treatment of actual MVST tanks, sludge wash solution is to be combined with tank supernate, and then treated.

The supernate/rinse from both surrogates was clear, tinted somewhat yellow (uranyl ion), and homogenous. QnD sludge was gray-pink and had the consistency of wet pancake batter. W23S sludge was bright yellow and also had a pancake batter consistency. A few larger particles were present that had a tendency to settle quickly after mixing. Pictures of the surrogate sludges and surrogate wash solutions (supernates), before and after, are presented in **Figures 4, 5, 6, 7, 8, 9, 10, 11**.

Results

Without any treatment, both surrogates failed to pass the TCLP test on 3 RCRA metals. With 'Optimum' treatment, the 'Quick and Dirty' surrogate passed (both the sludge and supernate-wash) TCLP. After 'Optimum' treatment, the W23 surrogate (W23S) sludge passed, but the supernate-wash did not pass. After 'Alternative' treatment, the supernate-wash from W23S still did not pass (failure in mercury limit). A matrix of pass/fails is shown below as **Table 1**. Individual test results/concentrations are discussed below. Pictures of the final products, with descriptions, may be found in **Figures 4, 5, 6, 7, 8, 9, 10,** and **11** at the end of this document.

Table 1. TCLP pass/failures of the various surrogate components after specific treatments. Each result is discussed in later sections. These pass/fail criteria only consider RCRA metals, not the radionuclide leach concentrations.

	Wet TCLP/Analysis	**Dried Waste Form (no additives)**	**Optimum Treatment**	**Alternative Treatment**
QnD Sludge	**Fail**	Not Tested	**Pass**	**Pass**
QnD Supernate	**Fail**	Not Tested	**Pass**	**Pass**
W23S Sludge	**Fail**	**Fail**	**Pass**	**Pass**
W23S Supernate	**Fail**	Not Tested	**Fail**	**Fail**

QnD Surrogate Results

A. Wet Results

After the two fractions (sludge and supernate-wash) were separated from the initial washing step, the untreated sludge was submitted for wet TCLP testing and the supernate was sent for ionic analysis. The sludge was found to fail chromium, lead, and mercury TCLP limits. The supernate, by calculation, was also found to fail in chromium, lead, and mercury. Of note was that a substantial amount of uranium remained soluble even at high pH. Supernate levels after a theoretical TCLP were >9 mgU/L. Wet results data can be found in **Tables 2** and **3** below.

Table 2. TCLP concentrations of metals and radionuclides for Quick and Dirty Surrogate Wet Sludge. Failing concentrations are bolded.

Component	**Measured Concentration (mg/L)**	**EPA Characteristic Limit Concentration (mg/L)**
Cadmium	0.001	1.0
Chromium	**11.69**	5.0
Mercury	**1.123**	0.2
Lead	**12.91**	5.0

Uranium	0.083	Not applicable
Thorium	<0.500	Not applicable

Table 3. Calculated TCLP concentrations of metals and radionuclides for Quick and Dirty surrogate supernate/rinse. Failing concentrations are bolded. Since TCLP does not technically apply to pure liquids, we used ionic analysis to simulate the FWENC drying process, followed by dissolution of the salts in the standard 20X TCLP leach volume that would be used. These calculations were only necessary for the initial wet tests of both surrogate washes.		
Component	**Calculated TCLP Leach Concentration (mg/L) based on ionic analysis**	**EPA Characteristic Limit Concentration (mg/L)**
Cadmium	<0.002	1.0
Chromium	**28.48**	5.0
Mercury	**1.522**	0.2
Lead	**26.50**	5.0
Uranium	9.19	Not applicable
Thorium	<0.500	Not applicable

B. QnD "Optimum" Formulation Results

Based on the above 'wet' results, the FWENC process requires that both the supernate and sludge be treated using the 'Optimum' formulation of additives. The treatment process worked well for both components of this surrogate, which passed TCLP requirements after treatment. **Tables 4** and **5** show leach concentrations from these tests. Additives had a profound effect on mercury in both the sludge and supernate-wash, reducing leachable concentration by several orders of magnitude. Other metals were also stabilized; concentrations of lead in the TCLP leaches were closer than any of the other metals to failure, at levels near 1 ppm (RCRA limit: 5 ppm).

Table 4. TCLP leach concentrations of metals and radionuclides for QnD stabilized sludge surrogate—Optimum Formulation (averages of triplicate TCLP). Failing concentrations are bolded.		
Component	**Measured Concentration (mg/L)**	**EPA Characteristic Limit Concentration (mg/L)**
Cadmium	<0.002	1.0
Chromium	0.539	5.0
Mercury	0.000091	0.2
Lead	0.862	5.0
Uranium	5.30	Not applicable
Thorium	1.67	Not applicable

Table 5. TCLP leach concentrations of metals and radionuclides for QnD stabilized supernate/rinse—Optimum Formulation. Failing concentrations are bolded.		
Component	**Measured Concentration (mg/L)**	**EPA Characteristic Limit Concentration (mg/L)**
Cadmium	0.009	1.0
Chromium	0.194	5.0

Mercury	0.000968	0.2
Lead	1.154	5.0
Uranium	0.409	Not applicable
Thorium	<0.500	Not applicable

C. QnD "Alternative" Formulation Results

Based on the above 'Optimum' results, the FWENC process diagram **DID NOT** require that the supernate and sludge be treated using the 'alternative' formulation of additives. Due to time constraints, 'optimum' and 'alternative' processing of surrogates were conducted in parallel, rather than sequentially as prescribed by the FWENC process. We present these data for completeness, and do not guarantee this level of testing for future hot tests. After the 'Alternative' treatment, the surrogate passed TCLP requirements on all four RCRA components. Data are shown in **Tables 6** and **7**.

Table 6. TCLP concentrations of metals and radionuclides for QnD stabilized surrogate—Alternative Formulation (averages of triplicate TCLP). Failing concentrations are bolded.

Component	Measured Concentration (mg/L)	EPA Characteristic Limit Concentration (mg/L)
Cadmium	0.016	1.0
Chromium	1.0557	5.0
Mercury	0.000352	0.2
Lead	1.409	5.0
Uranium	9.917	Not applicable
Thorium	4.907	Not applicable

Table 7. TCLP concentrations of metals and radionuclides for QnD stabilized supernate/rinse—Alternative Formulation (averages of triplicate TCLP). Failing concentrations are bolded.

Component	Measured Concentration (mg/L)	EPA Characteristic Limit Concentration (mg/L)
Cadmium	0.009	1.0
Chromium	0.174	5.0
Mercury	0.004187	0.2
Lead	1.225	5.0
Uranium	0.446	Not applicable
Thorium	<0.500	Not applicable

W23S Results

A. Wet Results

After the two fractions (sludge and supernate) were separated from the initial washing step, the untreated sludge was submitted for wet TCLP testing and the supernate was sent for ionic analysis. The sludge was found to fail mercury, chromium, and lead (see **Table 8** below). The supernate, by calculation, was also found to fail in chromium, lead, and mercury (see **Table 9** below).

Table 8. TCLP concentrations of metals and radionuclides for W23S surrogate wet sludge (averages of triplicate TCLP). Failing concentrations are bolded.		
Component	**Measured Concentration (mg/L)**	**EPA Characteristic Limit Concentration (mg/L)**
Cadmium	0.0059	1.0
Chromium	**17.524**	5.0
Mercury	**1.785**	0.2
Lead	**13.53**	5.0
Uranium	1.14	Not applicable
Thorium	1.662	Not applicable

Table 9. Theoretical leach TCLP concentrations of metals and radionuclides for W23S surrogate supernate/rinse (based on analysis of supernate; assumes complete dissolution). Failing concentrations are bolded. Since TCLP does not technically apply to pure liquids, we used ionic analysis to simulate the FWENC drying process, followed by dissolution of the salts in the standard 20X TCLP leach volume that would be used. These calculations were only necessary for the initial wet tests of both surrogate washes.		
Component	**Measured Concentration (mg/L)**	**EPA Characteristic Limit Concentration (mg/L)**
Cadmium	<0.002	1.0
Chromium	**24.026**	5.0
Mercury	**1.510**	0.2
Lead	**13.672**	5.0
Uranium	2.473	Not applicable
Thorium	<0.500	Not applicable

B. Dry Sludge Results

Although the FWENC process does not require dry, untreated sludge to be TCLP tested unless the wet sludge passes the test, we ran the dry test for comparative purposes to see what might be expected. Interestingly, the dry, untreated sludge failed only in mercury (see **Table 10** below).

Table 10. TCLP concentrations of metals and radionuclides for W23S Surrogate Dry Sludge—Untreated (averages of triplicate TCLP). Failing concentrations are bolded.		
Component	**Measured Concentration (mg/L)**	**EPA Characteristic Limit Concentration (mg/L)**
Cadmium	0.007	1.0
Chromium	2.717	5.0
Mercury	**0.621**	0.2
Lead	0.960	5.0
Uranium	0.110	Not applicable

Thorium	0.193	Not applicable

C. W23S "Optimum" Formulation Results

Based on the 'wet' results above, the FWENC process requires that both the supernate and sludge be treated using the 'optimum' formulation of additives. The sludge passed TCLP limits on the four RCRA metals. The supernate-wash failed in mercury. See **Tables 11** and **12** below for data/concentrations.

Table 11. TCLP concentrations of metals and radionuclides for W23S Stabilized Surrogate—Optimum Formulation (averages of triplicate TCLP). Failing concentrations are bolded.

Component	Measured Concentration (mg/L)	EPA Characteristic Limit Concentration (mg/L)
Cadmium	0.005	1.0
Chromium	0.379	5.0
Mercury	0.000702	0.2
Lead	0.861	5.0
Uranium	0.248	Not applicable
Thorium	0.222	Not applicable

Table12. TCLP concentrations of metals and radionuclides for W23S stabilized supernate—Optimum Formulation. Failing concentrations are bolded.

Component	Measured Concentration (mg/L)	EPA Characteristic Limit Concentration (mg/L)
Cadmium	<0.002	1.0
Chromium	0.367	5.0
Mercury	**0.267**	0.2
Lead	0.284	5.0
Uranium	1.51	Not applicable
Thorium	1.41	Not applicable

D. W23S "Alternative" Formulation Results

Based on the above results, the FWENC process requires that only the supernate-wash be treated using the 'alternative' formulation of additives. Since our experiments were conducted in parallel, we present the 'alternative' process on the sludge as well, and present both results below. The sludge passed easily, as expected. The supernate-wash, however, failed in mercury.

Table 13. TCLP concentrations of metals and radionuclides for W23S Stabilized Surrogate—Alternative Formulation (averages of triplicate TCLP). Failing concentrations are bolded.

Component	Measured Concentration (mg/L)	EPA Characteristic Limit Concentration (mg/L)
Cadmium	0.006	1.0
Chromium	0.455	5.0
Mercury	0.000655	0.2
Lead	0.972	5.0

Uranium	0.172	Not applicable
Thorium	1.037	Not applicable

Table 14. TCLP concentrations of metals and radionuclides for W23S stabilized supernate—Alternative Formulation (averages of triplicate TCLP). Failing concentrations are bolded.

Component	Measured Concentration (mg/L)	EPA Characteristic Limit Concentration (mg/L)
Cadmium	<0.002	1.0
Chromium	0.107	5.0
Mercury	**0.818***	0.2
Lead	<0.010	5.0
Uranium	1.51	Not applicable
Thorium	1.20	Not applicable

*Standard deviation on triplicate sample was 0.038.

Long Term Surrogate Studies With W23S

Work has been initiated for long term testing of the W23S surrogate. However, because the supernate-wash failed TCLP, we are storing this liquid until direction is given from FWENC for suitable treatment. We will proceed with testing of the W23S rinsed sludge.

UTS Considerations

Universal Treatment Standards/regulations (i.e., Land Disposal Restrictions) significantly affect the disposal criterion for many of the RCRA metals, some of which are listed in **Table 15** below. UTS limits are constituent-specific standards that apply generally to all wastes, rather than waste-specific standards that apply only to a specific waste stream. The amended UTS limits for characteristically toxic metal wastes established in the rule are generally more stringent than the characteristic levels. In addition, any underlying metal or organic hazardous constituents contained in these wastes must also be treated to meet the applicable Land Disposal Restriction standard, regardless of whether the concentration exceeds a TC threshold.

Table 15. Comparison of RCRA Versus UTS Criteria

Component	EPA Characteristic Limit Concentration (mg/L)	UTS
Cadmium	1.0	0.11
Chromium	5.0	0.6
Mercury	0.2	0.025
Lead	5.0	0.75

Uranium	Not applicable	Not applicable
Thorium	Not applicable	Not applicable

Based on the UTS criteria, neither the QnD nor W23S surrogates would pass after the prescribed FWENC treatments. Primary failure after treatment was in concentration of lead. A matrix of those results can be seen in Table 16.

Table 16. TCLP pass/failures of the various surrogate components after specific treatments based on UTS specifications. These pass/fail criteria only consider RCRA metals, not the radionuclide leach concentrations. Although the FWENC processes markedly reduced RCRA metals concentrations, they were not able to bring all metals below UTS limits.

	Wet TCLP/Analysis	Dried Waste Form (no additives)	Optimum Treatment	Alternative Treatment
QnD Sludge	**Fail (Pb, Cr, Hg)**	Not Tested	**Fail (Pb)**	**Fail (Pb, Cr)**
QnD Supernate	**Fail (Pb, Cr, Hg)**	Not Tested	**Fail (Pb)**	**Fail (Pb)**
W23S Sludge	**Fail (Pb, Cr, Hg)**	**Fail (Pb, Cr, Hg)**	**Fail (Pb)**	**Fail (Pb)**
W23S Supernate	**Fail (Pb, Cr, Hg)**	Not Tested	**Fail (Hg)**	**Fail (Hg)**

Relations to W-23 Tank Waste

W-23 tank samples are to be tested under the FWENC proposed treatment plan. Based on previous conflicting characterization data, is it still uncertain whether the proposed treatment will be effective. We believe that the chances of success under the 'Optimum' process are very good however, without assigning a specific probability factor.

Relations to MVST Characterization Data

Three of the MVST tank sludges failed a wet, untreated TCLP test even after washing. All untreated supernate washes failed TCLP. All failures were in Mercury. See **Table 17** below for the matrix. The FWENC procedure requires us to test the two worst sludges that failed, which were W-26 and W-27. These samples will be subjected to the 'Optimum' FWENC process. If our budget permits, we will perform dry, untreated TCLP measurements on the sludges from W-24, W-25, and W-28 during this FY (this is the process outlined by FWENC).

It is likely, based on surrogate testing, that the washed sludge will be stabilized by the 'Optimum' FWENC process such that it will be able to pass TCLP requirements. If UTS standards are applied however, at least one or two failures can be expected from the supernate-wash, which would probably be related to cadmium concentration.

Table 17. This table shows a matrix of MVST tanks and their pass/fail results from a wet TCLP of the sludge (after wash) and the supernate-wash itself (based on ionic concentrations/simulated evaporation/TCLP)		
MVST Tank	**Wet TCLP**	**Supernate-wash**
W-24	**Pass**	**Fail**
W-25	**Pass**	**Fail**
W-26	**Fail**	**Fail**
W-27	**Fail**	**Fail**
W-28	**Pass**	**Fail**
W-31	**Fail**	**Fail**

Physical Considerations

Dried sludge surrogates having undergone the FWENC treatment process had the texture of soft chalk; these materials could be ground easily into a fine powder. Dried supernate/rinse from the surrogates formed hard crystals. In both supernate and sludge cases, the act of drying caused some chemical separation to occur in the samples, noticeably visible as stratification or layering in the dried samples.

Vacuum-assisted drying of supernate liquids at 80^{o}C took several days for open-faced containers, primarily due to the lack of convection with the vacuum oven. Any additional airspace convection that can be generated during treatment will speed the drying process considerably.

Additional Information

Requests for additional information regarding the contents of this report or other results from this work should be directed Ms. Jacquie Noble-Dial at (865) 241-6184 or NobleDialJR@oro.doe.gov

Figure 1. Flowchart of FWENC treatment process for washed sludge.

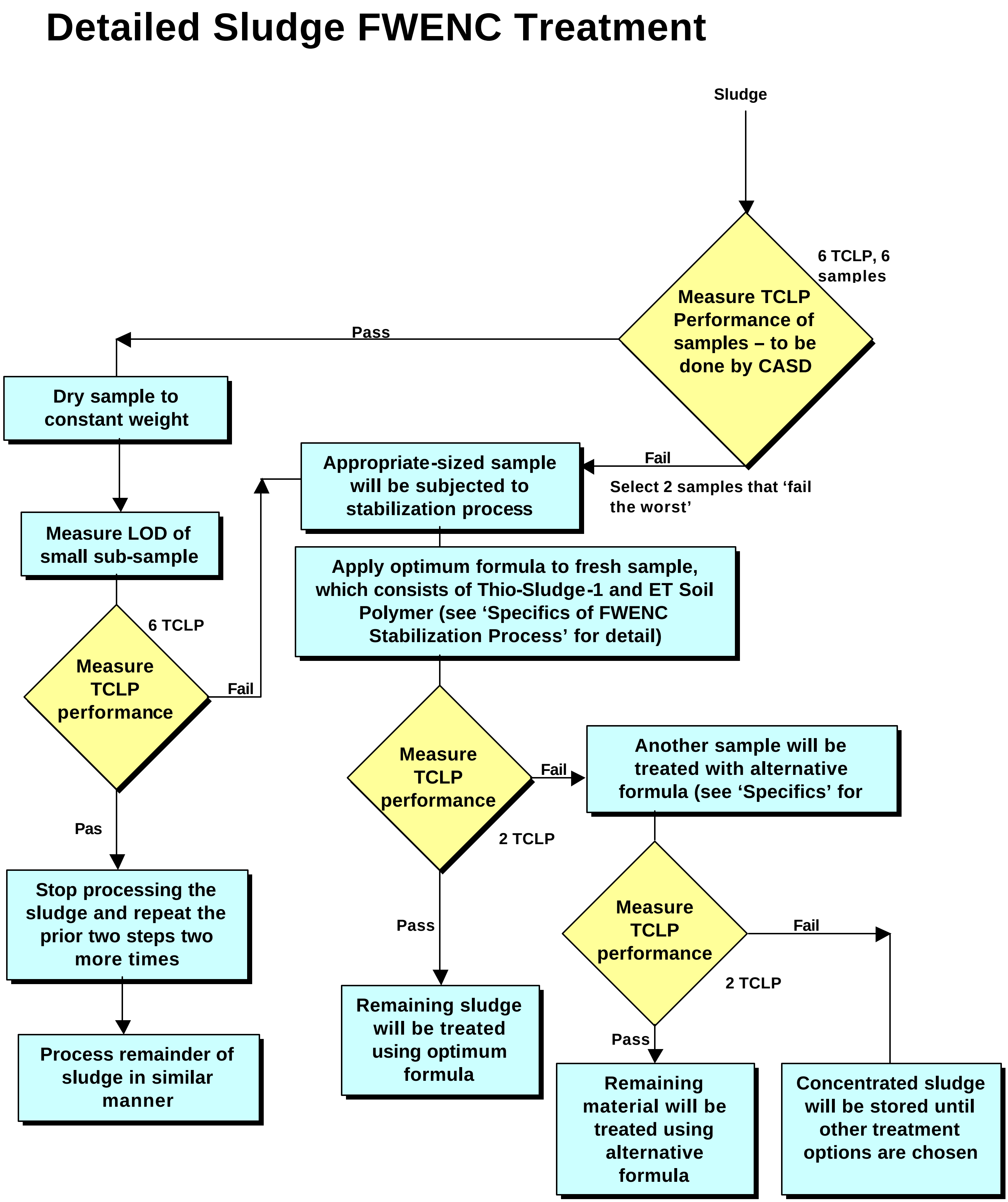


Figure 2. Flowchart of FWENC treatment process for supernate-wash

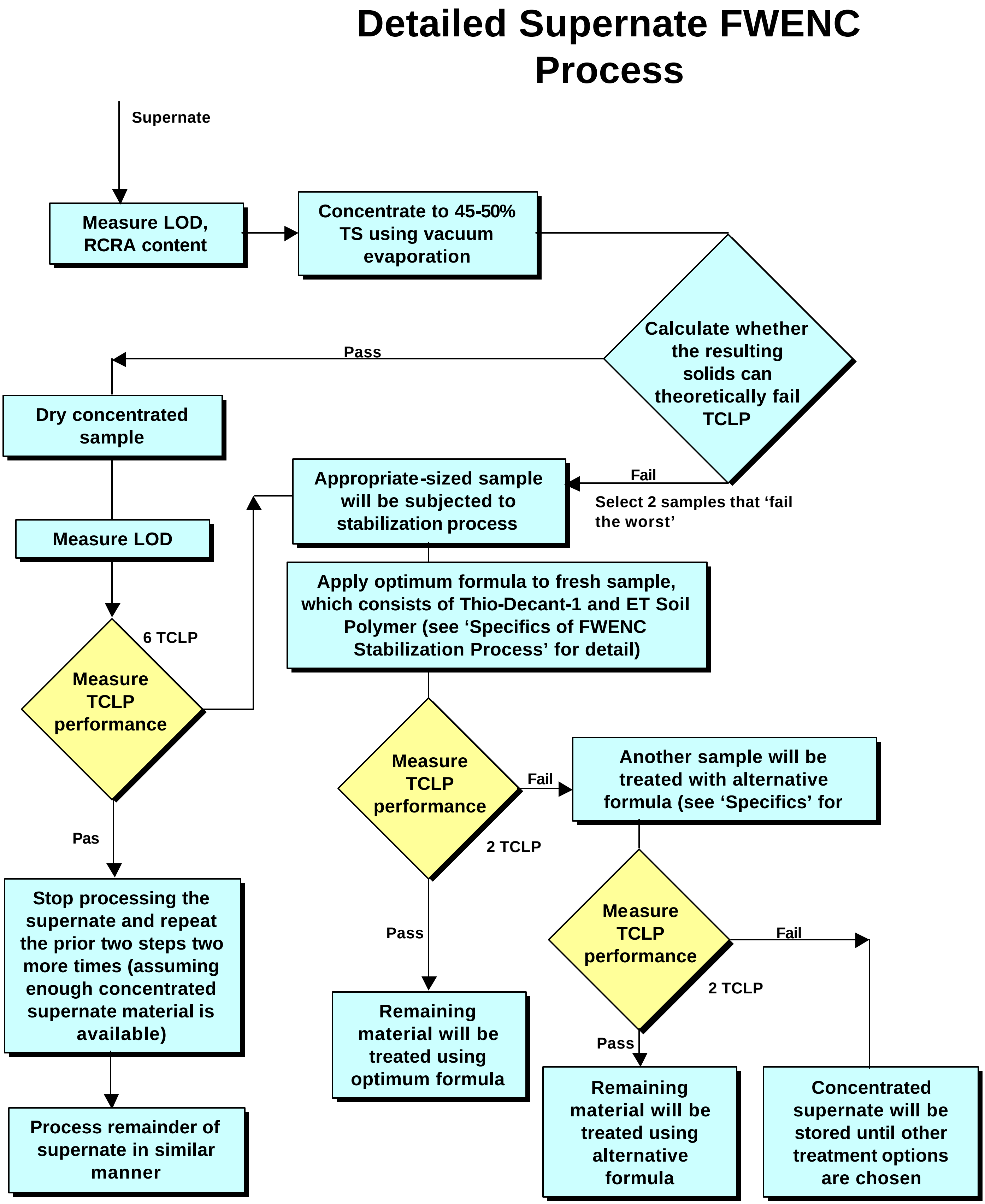
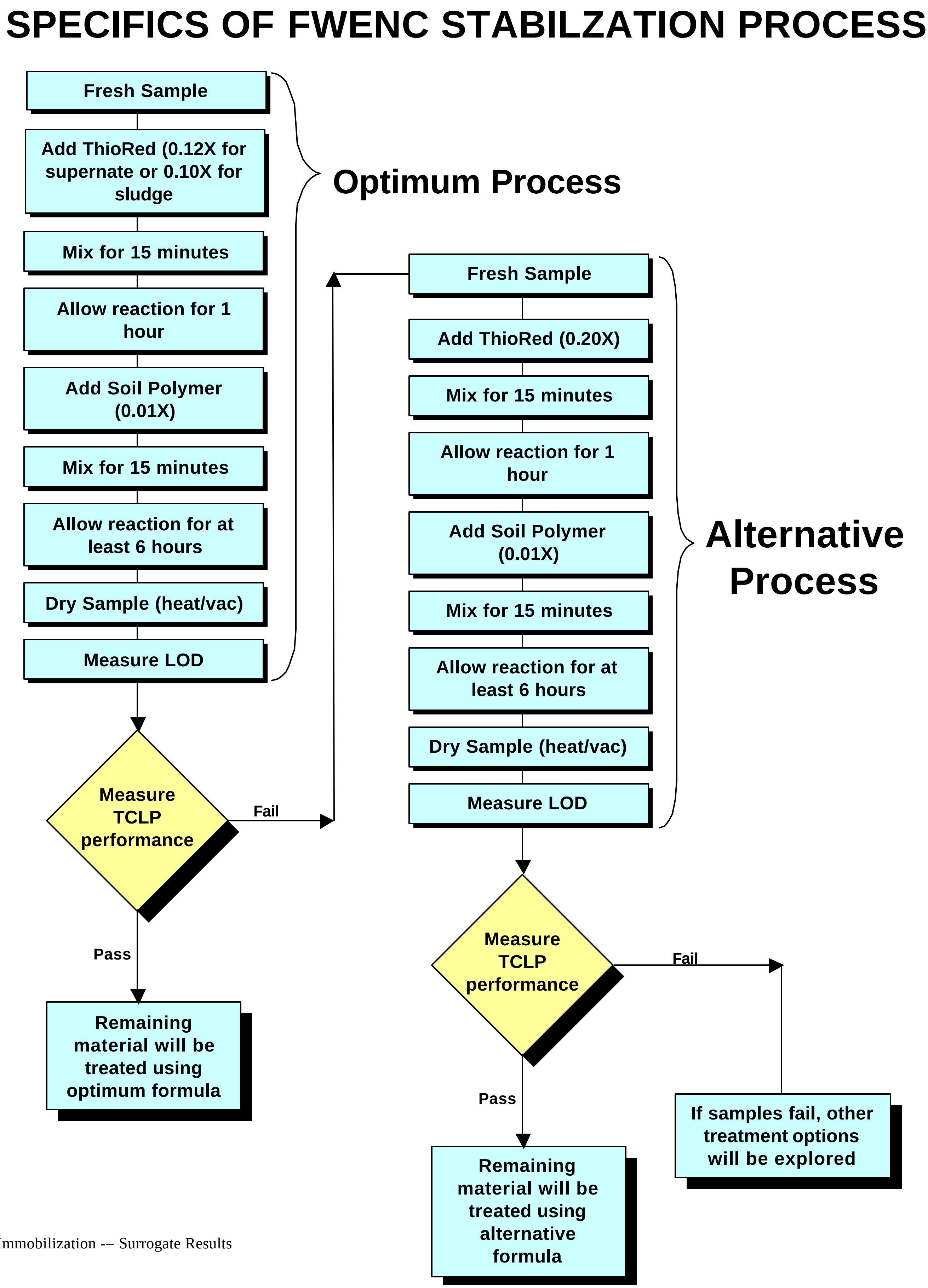


Figure 3. Flowchart of chemical additive processing for the FWENC process.



FIGURES

Figure 4a. Quick and Dirty Surrogate
Figure 4b. QnD during wash/settling
Figure 4c. QnD after 12 hours of settling

Figure 5a. Rinsed QnD sludge after FWENC additives, before drying
Figure 5b. Rinsed QnD sludge after FWENC additives, after drying
Figure 5c. Rinsed QnD sludge after FWENC additives, after drying, top view

Figure 6a. QnD supernate, untreated
Figure 6b. QnD supernate, after FWENC additive treatment, before drying

Figure 7a. QnD supernate, treated, after drying
Figure 7b. QnD supernate, treated, after drying, top view

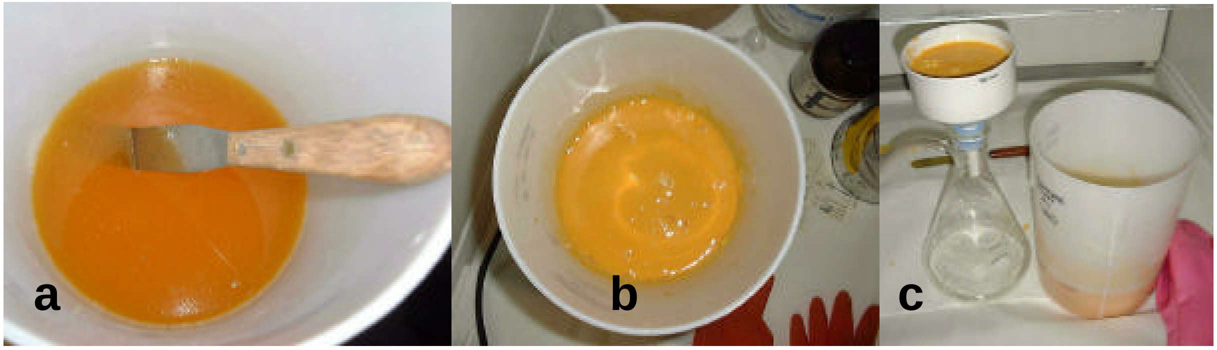


Figure 8a. Preparation of W23S surrogate; mixture before precipitation
Figure 8b. Preparation of W23S surrogate; mixture after precipitation
Figure 8c. Preparation of W23S surrogate; filtration/rinse of precipitant

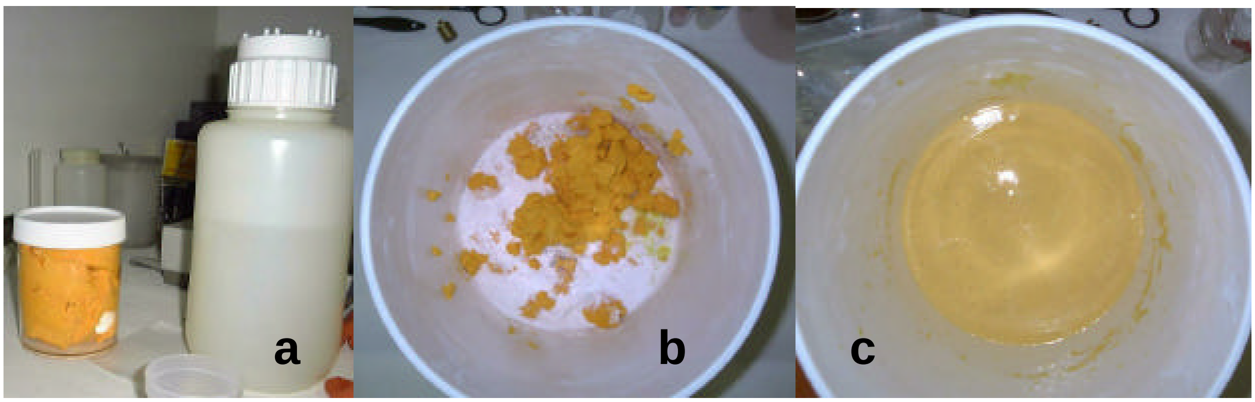


Figure 9a. Preparation of W23S; filter cake and rinse
Figure 9b. Preparation of W23S; addition of chemicals to filter cake
Figure 9c. Final W23S surrogate

Figure 10a. Wash of W23S surrogate
Figure 10b. Sludge from W23S before FWENC treatment
Figure 10c. Treated W23S sludge, before drying

Figure 11a. Treated W23S sludge after drying
Figure 11b. Treated W23S sludge after drying, top view
Figure 11c. Treated W23S sludge, stratification

Appendix A

QnD – Quick and Dirty Surrogate Characterization and Comparison		
Component	**Surrogate Concentration (mg/kg surrogate)**	**W-23 Sample Measured Concentration (mg/kg waste)**
Cadmium	51	24
Chromium	352	161
Mercury	76	35
Lead	1,539	705
Aluminum	3,777	1,730
Calcium	124,236	56,900
TIC	14,399	1,320
Iron	3,777	1,730
Potassium	28,166	12,900
Magnesium	23,799	10,900
Sodium	127,074	58,200
Nitrate	174,236	79,800
Nitrite	18,537	8,490
Chlorine	11,397	5,220
Fluorine	1,777	814
Sulfate	19,891	9,110
Strontium	600	275
Thorium	35,808	16,400
Uranium	17,445	7,990
Silicon	4,672	2,140
TOC	6,253	1,550

Appendix B

W23S – Representative Surrogate Characterization and Comparison		
Component	Surrogate Concentration (mg/kg surrogate)	W-23 Sample Measured Concentration (mg/kg waste)
Cadmium	24	24
Chromium	161	161
Mercury	37	35
Lead	711	705
Aluminum	1729	1730
Calcium	56593	56900
Iron	1754	1730
Sulfate	9170	9110
Potassium	12838	12900
Nitrite	8416	8490
Magnesium	10779	10900
Sodium	58613	58200
Chloride	5151	5220
Fluoride	803	814
Silicon	2134	2140
Strontium	277	275
Nitrate	79143	79800
Thorium	16710	16400
Uranium	8134	7990
TOC	1550	1550

ORNL IMMOBILIZATION:
Surrogate Results

OR00WT31, 3TKH

John Barton
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September 29, 2000

SUMMARY: This document contains results from studies conducted for verification of a FWENC-proposed stabilization process for treating Oak Ridge Reservation tank wastes. Two surrogate and seven actual tank wastes are being used in this study. Without any treatment, both surrogates failed TCLP EPA limits on three RCRA metals. Using the 'Optimum' formulation provided by FWENC, both rinsed tank sludge surrogates were stabilized and passed TCLP. The supernate/wash/rinse from one surrogate passed TCLP after 'Optimum' treatment; the supernate/wash/rinse from a more representative surrogate failed TCLP (in mercury) after both an 'Optimum' and an 'Alternative' treatment. Both surrogates failed to reach Universal Treatment Standard limits after both 'Optimum' and 'Alternative' treatments. Based on initial characterization of W23 and MVST tank sludges, it is likely that the FWENC 'Optimum' treatment will stabilize actual tank contents to TCLP EPA limits. It may be possible to reach UTS limits as well, particularly on the rinsed sludges.

Introduction

This report details results-to-date from stabilization studies of two different surrogate tank wastes and seven actual wastes. The stabilization process used was developed by Foster Wheeler Environmental Corporation (FWENC) and combines techniques of sluicing, dehydration, and stabilizer addition steps to achieve a final solid waste product that no longer displays the characteristic of toxicity as outlined in 40 CFR 261.24.

Background. Oak Ridge and Idaho have hundreds of thousands of gallons of low-level mixed waste in underground storage tanks that must be treated for disposal. This work addresses the joint Oak Ridge and Idaho concern for stabilization of hazardous components within their immobilized waste forms, and evaluates the approach taken by the private vendor, Foster Wheeler for immobilization of OR waste. ORNL is conducting both immediate and longer-term leach testing to ensure that the waste forms retain the hazardous metals and meet RCRA LDR limits. Since storage on site may occur prior to shipment to the Waste Isolation Pilot Plant (WIPP) or the Nevada Test Site (NTS), it is important to confirm that the waste form remains stable over time and will meet TCLP LDR limits at time of shipment. ORNL has initiated long term testing of both simulated and actual waste streams (begun in FY00) and completed initial processing of surrogates and several actual wastes (begun in FY00) using the FWENC-proposed process.

Need and Problem Descriptions. Refer to technical response A9719 in the TFA FY2002 Site Needs Assessment for descriptions of the site needs, functional requirements, and problem statements. The Site Needs Assessment is located on the TFA Technical Team home page (http://www.pnl.gov/tfa/program/needs00). TFA2001 – FY2003 Technical Responses may be found on the TFA Technical Team home page (http://www.pnl.gov/tfa/program/fy01techresp).

Toxicity Characteristic. Toxicity of a waste is measured as the potential for the toxic constituents in the waste to leach out and contaminate groundwater at levels of concern to human health and the environment. To determine if a waste exhibits the toxicity characteristic, constituents are extracted in a procedure that simulates leaching action in municipal landfills (Toxic Characteristic Leaching Procedure [TCLP], EPA Test Method 1311). Details regarding the Toxicity Characteristic as defined by EPA can be found at http://www.epa.gov/docs/epacfr40/chapt-I.info/subch-I/40P0261.pdf; details regarding the TCLP method can be found at http://oecdwsrv.oecd.ornl.gov/landerin/epb006.html

Methods

FWENC Process. The FWENC process is diagrammed in **Figures 1**, **2**, and **3**, which can be found at the end of this document. Tank surrogates and actual wastes are first washed with 5 parts water to 1 part wet sludge and allowed to settle. This generates two fractions, referred to as 'sludge' (settled solids) and 'supernate' (decanted liquid) in this report. Samples from each fraction are tested to determine whether the fraction displays, or will display, the toxicity characteristic in its final dehydrated form. If either fraction fails to pass, then samples from that fraction are treated using an 'optimum' formulation of chemical additives, and then retested for toxicity characteristics. If this treatment fails, an 'alternative' formulation is used to treat another set of samples, followed by a toxicity analysis.

Surrogates. Two surrogates were used in this study. One is referred to as QnD (Quick and Dirty) surrogate, while the other is called 'W23S', a highly representative surrogate for W23 Tank waste. The QnD surrogate formulation had been used in prior treatability studies of W23 tank wastes. This surrogate was prepared by simple mixing of RCRA, process, and radionuclide metals together to generate a rough simulation of the composition of tank wastes. A more representative surrogate, W23S, was prepared by mixing RCRA, process, and radionuclide metal compounds, mainly nitrates, together followed by a sodium hydroxide precipitation of the component metals. A volume of water 1.5 times larger than the volume of the precipitated mixture was then used to remove soluble salts from the precipitate. The resulting filter cake and liquid filtrate were re-analyzed for both cation and anion components. The solids were then amended with the necessary amounts of requisite chemicals, including water, to bring the final composition to within 2% (weight fraction) of actual W23 tank waste composition in more than 20 major constituents (both anion and cation). This surrogate was designed specifically for the actual W23 sludge sample to be used in hot testing. **Appendices A** and **B** contain the ionic constituents and their concentrations for both surrogates and the W23 sludge sample. Note that although we are defining the sludge wash as 'supernate', no actual tank supernates or surrogate tank supernates were tested in this phase of the work. During FWENC treatment of actual MVST tanks, however, sludge wash solution is to be combined with tank supernate, and then treated.

The supernate/rinse from both surrogates was clear, tinted somewhat yellow (uranyl ion), and homogenous. QnD sludge was gray-pink and had the consistency of wet pancake batter. W23S sludge was bright yellow and also had a pancake batter consistency. A few larger particles were present that had a tendency to settle quickly after mixing. Pictures of the surrogate sludges and surrogate wash solutions (supernates), before and after, are presented in **Figures 4, 5, 6, 7, 8, 9, 10, 11**.

Actual Wastes. Tests were initiated on seven different actual tank wastes, including W23 and Melton Valley Storage Tanks (MVSTs) W24, W25, W26, W27, W28, and W31. The MVST work, although not intended to start until FY01, was accelerated due to the OR user schedule. After characterization, the FWENC 'optimum' process (as described previously, and in **Figures 1, 2, 3**) was applied to the two worst-failing MVST tank samples and also to W23 tank waste. That phase of the work is not complete and will continue into FY01.

Surrogate Results

Without any treatment, both surrogates failed to pass the TCLP test on 3 RCRA metals. With 'Optimum' treatment, the 'Quick and Dirty' surrogate passed (both the sludge and supernate-wash) TCLP. After 'Optimum' treatment, the W23 surrogate (W23S) sludge passed, but the supernate-wash did not pass. After 'Alternative' treatment, the supernate-wash from W23S still did not pass (failure in mercury limit). A matrix of pass/fails is shown below as **Table 1**. Individual test results/concentrations are discussed below. Pictures of the final products, with descriptions, may be found in **Figures 4, 5, 6, 7, 8, 9, 10,** and **11** at the end of this document.

Table 1. TCLP pass/failures of the various surrogate components after specific treatments. Each result is discussed in later sections. These pass/fail criteria only consider RCRA metals, not the radionuclide leach concentrations.

	Wet TCLP/Analysis	Dried Waste Form (no additives)	Optimum Treatment	Alternative Treatment
QnD Sludge	**Fail**	Not Tested	**Pass**	**Pass**
QnD Supernate	**Fail**	Not Tested	**Pass**	**Pass**
W23S Sludge	**Fail**	**Fail**	**Pass**	**Pass**
W23S Supernate	**Fail**	Not Tested	**Fail**	**Fail**

QnD Surrogate Results

A. Wet Results

After the two fractions (sludge and supernate-wash) were separated from the initial washing step, the untreated sludge was submitted for wet TCLP testing and the supernate was sent for ionic analysis. The sludge was found to fail chromium, lead, and mercury TCLP limits. The supernate, by calculation, was also found to fail in chromium, lead, and mercury. Of note was that a substantial amount of uranium remained suspended/soluble even at high pH. Supernate levels after a theoretical TCLP were >9 mgU/L. Wet results data can be found in **Tables 2** and **3** below.

Table 2. TCLP concentrations of metals and radionuclides for Quick and Dirty Surrogate Wet Sludge. Failing concentrations are bolded.

Component	Measured Concentration (mg/L)	EPA Characteristic Limit Concentration (mg/L)
Cadmium	0.001	1.0
Chromium	**11.69**	5.0
Mercury	**1.123**	0.2
Lead	**12.91**	5.0
Uranium	0.083	Not applicable
Thorium	<0.500	Not applicable

Table 3. Calculated TCLP concentrations of metals and radionuclides for Quick and Dirty surrogate supernate/rinse. Failing concentrations are bolded. Since TCLP does not technically apply to pure liquids, we used ionic analysis to simulate the FWENC drying process, followed by dissolution of the salts in the standard 20X TCLP leach volume that would be used. These calculations were only necessary for the initial wet tests of both surrogate washes.

Component	Calculated TCLP Leach Concentration (mg/L) based on ionic analysis	EPA Characteristic Limit Concentration (mg/L)
Cadmium	<0.002	1.0
Chromium	**28.48**	5.0
Mercury	**1.522**	0.2
Lead	**26.50**	5.0
Uranium	9.19	Not applicable

Thorium	<0.500	Not applicable

B. QnD "Optimum" Formulation Results

Based on the above 'wet' results, the FWENC process requires that both the supernate and sludge be treated using the 'Optimum' formulation of additives. The treatment process worked well for both components of this surrogate, which passed TCLP requirements after treatment. **Tables 4** and **5** show leach concentrations from these tests. Additives had a profound effect on mercury in both the sludge and supernate-wash, reducing leachable concentration by several orders of magnitude. Other metals were also stabilized; concentrations of lead in the TCLP leaches were closer than any of the other metals to failure, at levels near 1 ppm (RCRA limit: 5 ppm).

Table 4. TCLP leach concentrations of metals and radionuclides for QnD stabilized sludge surrogate—Optimum Formulation (averages of triplicate TCLP). Failing concentrations are bolded.

Component	Measured Concentration (mg/L)	EPA Characteristic Limit Concentration (mg/L)
Cadmium	<0.002	1.0
Chromium	0.539	5.0
Mercury	0.000091	0.2
Lead	0.862	5.0
Uranium	5.30	Not applicable
Thorium	1.67	Not applicable

Table 5. TCLP leach concentrations of metals and radionuclides for QnD stabilized supernate/rinse—Optimum Formulation. Failing concentrations are bolded.

Component	Measured Concentration (mg/L)	EPA Characteristic Limit Concentration (mg/L)
Cadmium	0.009	1.0
Chromium	0.194	5.0
Mercury	0.000968	0.2
Lead	1.154	5.0
Uranium	0.409	Not applicable
Thorium	<0.500	Not applicable

C. QnD "Alternative" Formulation Results

Based on the above 'Optimum' results, the FWENC process diagram **DID NOT** require that the supernate and sludge be treated using the 'alternative' formulation of additives. Due to time constraints, 'optimum' and 'alternative' processing of surrogates were conducted in parallel, rather than sequentially as prescribed by the FWENC process. We present these data for completeness, and do not guarantee this level of testing for future hot tests. After the 'Alternative' treatment, the surrogate passed TCLP requirements on all four RCRA components. Data are shown in **Tables 6** and **7**.

Table 6. TCLP concentrations of metals and radionuclides for QnD stabilized surrogate—Alternative Formulation (averages of triplicate TCLP). Failing concentrations are bolded.		
Component	**Measured Concentration (mg/L)**	**EPA Characteristic Limit Concentration (mg/L)**
Cadmium	0.016	1.0
Chromium	1.0557	5.0
Mercury	0.000352	0.2
Lead	1.409	5.0
Uranium	9.917	Not applicable
Thorium	4.907	Not applicable

Table 7. TCLP concentrations of metals and radionuclides for QnD stabilized supernate/rinse—Alternative Formulation (averages of triplicate TCLP). Failing concentrations are bolded.		
Component	**Measured Concentration (mg/L)**	**EPA Characteristic Limit Concentration (mg/L)**
Cadmium	0.009	1.0
Chromium	0.174	5.0
Mercury	0.004187	0.2
Lead	1.225	5.0
Uranium	0.446	Not applicable
Thorium	<0.500	Not applicable

W23S Results

A. Wet Results

After the two fractions (sludge and supernate) were separated from the initial washing step, the untreated sludge was submitted for wet TCLP testing and the supernate was sent for ionic analysis. The sludge was found to fail mercury, chromium, and lead (see **Table 8** below). The supernate, by calculation, was also found to fail in chromium, lead, and mercury (see **Table 9** below).

Table 8. TCLP concentrations of metals and radionuclides for W23S surrogate wet sludge (averages of triplicate TCLP). Failing concentrations are bolded.		
Component	**Measured Concentration (mg/L)**	**EPA Characteristic Limit Concentration (mg/L)**
Cadmium	0.0059	1.0
Chromium	**17.524**	5.0
Mercury	**1.785**	0.2
Lead	**13.53**	5.0
Uranium	1.14	Not applicable
Thorium	1.662	Not applicable

Table 9. Theoretical leach TCLP concentrations of metals and radionuclides for W23S surrogate supernate/rinse (based on analysis of supernate; assumes complete dissolution). Failing concentrations are bolded. Since TCLP does not technically apply to pure liquids, we used ionic analysis to simulate the FWENC drying process, followed by dissolution of the salts in the standard 20X TCLP leach volume that would be used. These calculations were only necessary for the initial wet tests of both surrogate washes.

Component	Measured Concentration (mg/L)	EPA Characteristic Limit Concentration (mg/L)
Cadmium	<0.002	1.0
Chromium	**24.026**	5.0
Mercury	**1.510**	0.2
Lead	**13.672**	5.0
Uranium	2.473	Not applicable
Thorium	<0.500	Not applicable

B. Dry Sludge Results

Although the FWENC process does not require dry, untreated sludge to be TCLP tested unless the wet sludge passes the test, we ran the dry test for comparative purposes to see what might be expected. Interestingly, the dry, untreated sludge failed only in mercury (see **Table 10** below).

Table 10. TCLP concentrations of metals and radionuclides for W23S Surrogate Dry Sludge—Untreated (averages of triplicate TCLP). Failing concentrations are bolded.

Component	Measured Concentration (mg/L)	EPA Characteristic Limit Concentration (mg/L)
Cadmium	0.007	1.0
Chromium	2.717	5.0
Mercury	**0.621**	0.2
Lead	0.960	5.0
Uranium	0.110	Not applicable
Thorium	0.193	Not applicable

C. W23S "Optimum" Formulation Results

Based on the 'wet' results above, the FWENC process requires that both the supernate and sludge be treated using the 'optimum' formulation of additives. The sludge passed TCLP limits on the four RCRA metals. The supernate-wash failed in mercury. See **Tables 11** and **12** below for data/concentrations.

Table 11. TCLP concentrations of metals and radionuclides for W23S Stabilized Surrogate—Optimum Formulation (averages of triplicate TCLP). Failing concentrations are bolded.		
Component	**Measured Concentration (mg/L)**	**EPA Characteristic Limit Concentration (mg/L)**
Cadmium	0.005	1.0
Chromium	0.379	5.0
Mercury	0.000702	0.2
Lead	0.861	5.0
Uranium	0.248	Not applicable
Thorium	0.222	Not applicable

Table12. TCLP concentrations of metals and radionuclides for W23S stabilized supernate—Optimum Formulation. Failing concentrations are bolded.		
Component	**Measured Concentration (mg/L)**	**EPA Characteristic Limit Concentration (mg/L)**
Cadmium	<0.002	1.0
Chromium	0.367	5.0
Mercury	**0.267**	0.2
Lead	0.284	5.0
Uranium	1.51	Not applicable
Thorium	1.41	Not applicable

D. W23S "Alternative" Formulation Results

Based on the above results, the FWENC process requires that only the supernate-wash be treated using the 'alternative' formulation of additives. Since our experiments were conducted in parallel, we present the 'alternative' process on the sludge as well, and present both results below. The sludge passed easily, as expected. The supernate-wash, however, failed in mercury.

Table 13. TCLP concentrations of metals and radionuclides for W23S Stabilized Surrogate—Alternative Formulation (averages of triplicate TCLP). Failing concentrations are bolded.		
Component	**Measured Concentration (mg/L)**	**EPA Characteristic Limit Concentration (mg/L)**
Cadmium	0.006	1.0
Chromium	0.455	5.0
Mercury	0.000655	0.2
Lead	0.972	5.0
Uranium	0.172	Not applicable
Thorium	1.037	Not applicable

Table 14. TCLP concentrations of metals and radionuclides for W23S stabilized supernate—Alternative Formulation (averages of triplicate TCLP). Failing concentrations are bolded.		
Component	**Measured Concentration (mg/L)**	**EPA Characteristic Limit Concentration (mg/L)**
Cadmium	<0.002	1.0
Chromium	0.107	5.0
Mercury	**0.818***	0.2
Lead	<0.010	5.0
Uranium	1.51	Not applicable
Thorium	1.20	Not applicable

*Standard deviation on triplicate sample was 0.038.

Long Term Surrogate Studies With W23S

Work has been initiated for long term testing of the W23S surrogate. However, because the supernate-wash failed TCLP, we are storing this liquid until direction is given from FWENC for suitable treatment. We have proceeded with testing of the W23S rinsed sludge.

UTS Considerations

Universal Treatment Standards/regulations (i.e., Land Disposal Restrictions) significantly affect the disposal criterion for many of the RCRA metals, some of which are listed in **Table 15** below. UTS limits are constituent-specific standards that apply generally to all wastes, rather than waste-specific standards that apply only to a specific waste stream. The amended UTS limits for characteristically toxic metal wastes established in the rule are generally more stringent than the characteristic levels. In addition, any underlying metal or organic hazardous constituents contained in these wastes must also be treated to meet the applicable Land Disposal Restriction standard, regardless of whether the concentration exceeds a TC threshold.

Table 15. Comparison of RCRA Versus UTS Criteria		
Component	**EPA Characteristic Limit Concentration (mg/L)**	**UTS**
Cadmium	1.0	0.11
Chromium	5.0	0.6
Mercury	0.2	0.025
Lead	5.0	0.75
Uranium	Not applicable	Not applicable
Thorium	Not applicable	Not applicable

Based on the UTS criteria, neither the QnD nor W23S surrogates would pass after the prescribed FWENC treatments. Primary failure after treatment was in concentration of lead. A matrix of those results can be seen in Table 16.

Table 16. TCLP pass/failures of the various surrogate components after specific treatments based on UTS specifications. These pass/fail criteria only consider RCRA metals, not the radionuclide leach concentrations. Although the FWENC processes markedly reduced RCRA metals concentrations, they were not able to bring all metals below UTS limits.				
	Wet TCLP/Analysis	**Dried Waste Form (no additives)**	**Optimum Treatment**	**Alternative Treatment**
QnD Sludge	**Fail (Pb, Cr, Hg)**	Not Tested	**Fail (Pb)**	**Fail (Pb, Cr)**
QnD Supernate	**Fail (Pb, Cr, Hg)**	Not Tested	**Fail (Pb)**	**Fail (Pb)**
W23S Sludge	**Fail (Pb, Cr, Hg)**	**Fail (Pb, Cr, Hg)**	**Fail (Pb)**	**Fail (Pb)**
W23S Supernate	**Fail (Pb, Cr, Hg)**	Not Tested	**Fail (Hg)**	**Fail (Hg)**

Actual Waste Results

W23 Tank Waste

Triplicate W23 tank samples have been treated using the FWENC proposed treatment plan. The final analytical results were not finished at the time this report was written and are expected in early FY01. Pictures of the final waste form, treated with the 'Optimum' formula, are shown as **Figures 12** and **14**.

MVST Tanks Waste

Three of the six MVST tank sludges failed a wet, untreated TCLP test even after washing. All untreated supernate washes failed TCLP. All failures were in Mercury. See **Table 17** below for the matrix. The FWENC procedure requires us to test the two worst sludges that failed, which were W26 and W27. These samples have been subjected to the 'Optimum' FWENC process. We have also performed dry, untreated TCLP measurements on the sludges from W24, W25, and W28 during this FY (as outlined by FWENC treatment strategy). None of the analytical results were available from these tests at the time this report was written, but are expected in early FY01. Pictures of the final treated waste forms for the five MVST samples are shown in **Figures 12, 13,** and **14**.

It is likely, based on surrogate testing, that the washed sludge will be stabilized by the 'Optimum' FWENC process such that it will be able to pass TCLP requirements. If UTS standards are applied however, at least one or two failures can be expected from the supernate-wash, which would probably be related to cadmium concentration.

Table 17. This table shows a matrix of MVST tanks and their pass/fail results from a wet TCLP of the sludge (after wash) and the supernate-wash itself (based on ionic concentrations/simulated evaporation/TCLP)		
MVST Tank	**Wet TCLP**	**Supernate-wash**
W-24	**Pass**	**Fail**
W-25	**Pass**	**Fail**
W-26	**Fail**	**Fail**

W-27	**Fail**	**Fail**
W-28	**Pass**	**Fail**
W-31	**Fail**	**Fail**

Physical Considerations

Dried sludge surrogates having undergone the FWENC treatment process had the texture of soft chalk; these materials could be ground easily into a fine powder. Dried supernate/rinse from the surrogates formed hard crystals. In both supernate and sludge cases, the act of drying caused some chemical separation to occur in the samples, noticeably visible as stratification or layering in the dried samples.

Vacuum-assisted drying of supernate liquids at 80^{o}C took several days for open-faced containers, primarily due to the lack of convection with the vacuum oven. Any additional airspace convection that can be generated during treatment will speed the drying process considerably.

The final dried waste product from MVST Tank W28 looked very different from the other stabilized forms. Upon drying, it was granular, and did not form a 'cake' as did the other tank samples. Pictures of these dried samples can be found in **Figures 12, 13,** and **14.**

Additional Information

Requests for additional information regarding the contents of this report or other results from this work should be directed to Mr. Daryl Green at (865) 241-6198 or greendd@oro.doe.gov

Figure 1. Flowchart of FWENC treatment process for washed sludge.

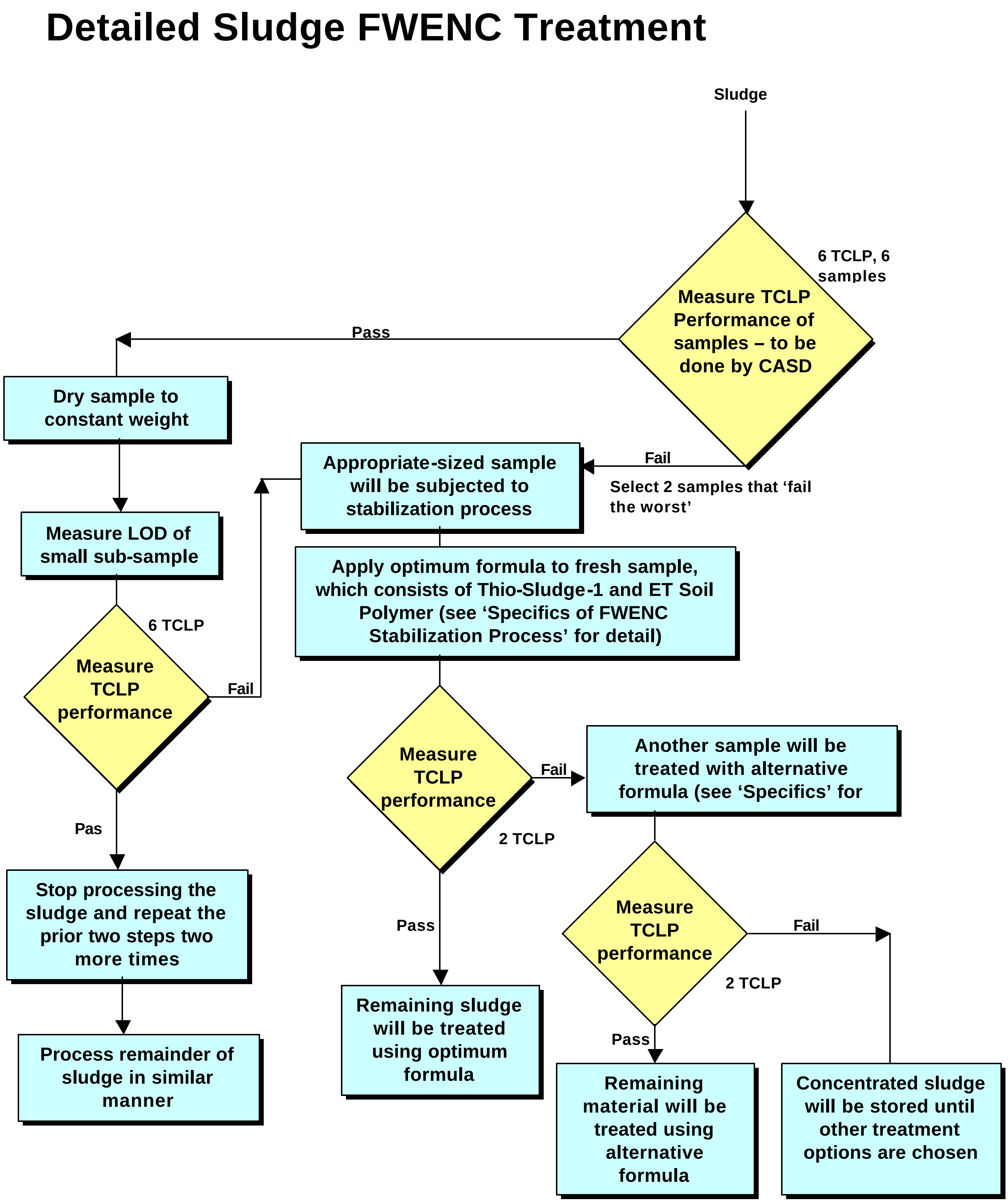


Figure 2. Flowchart of FWENC treatment process for supernate-wash

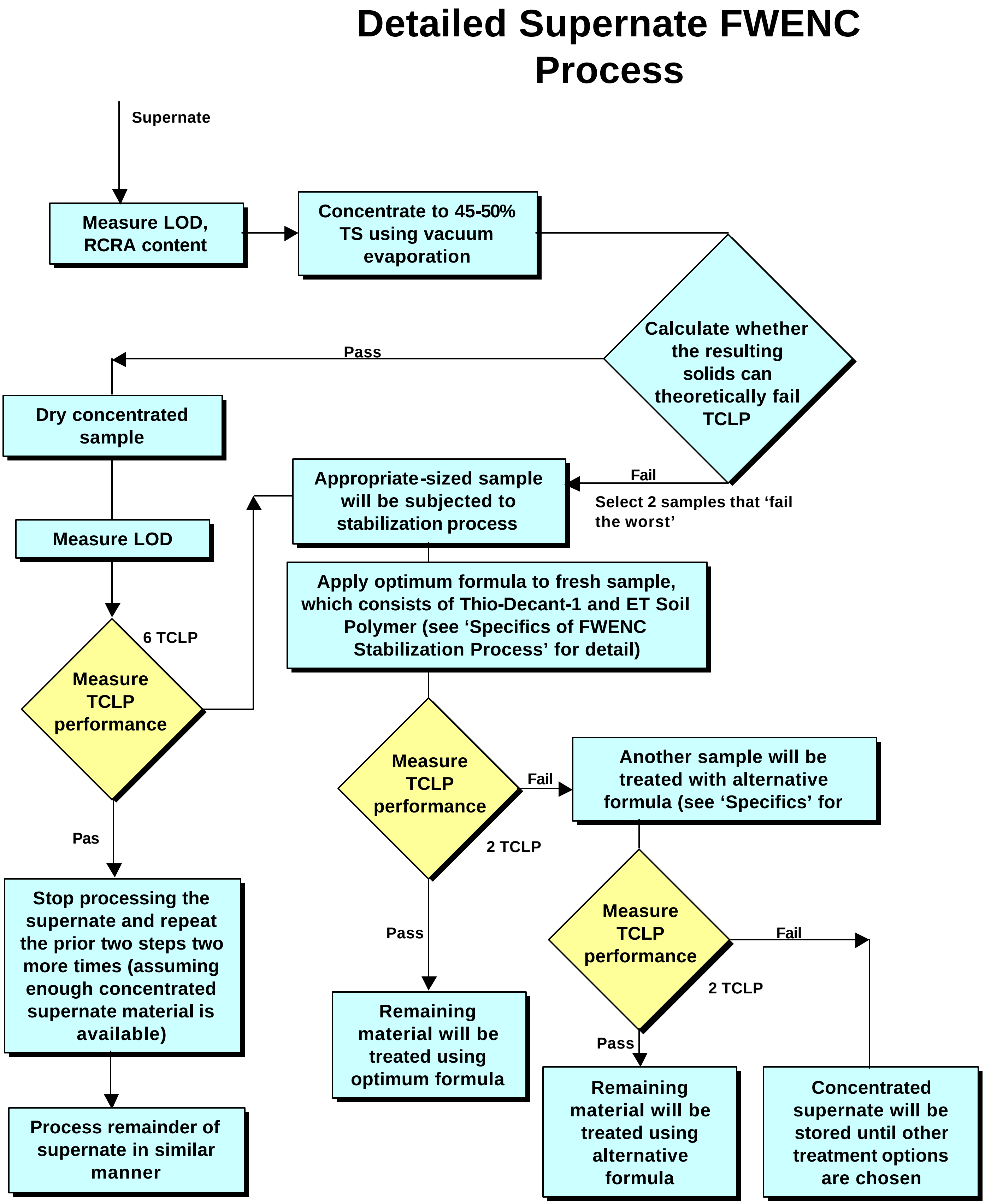
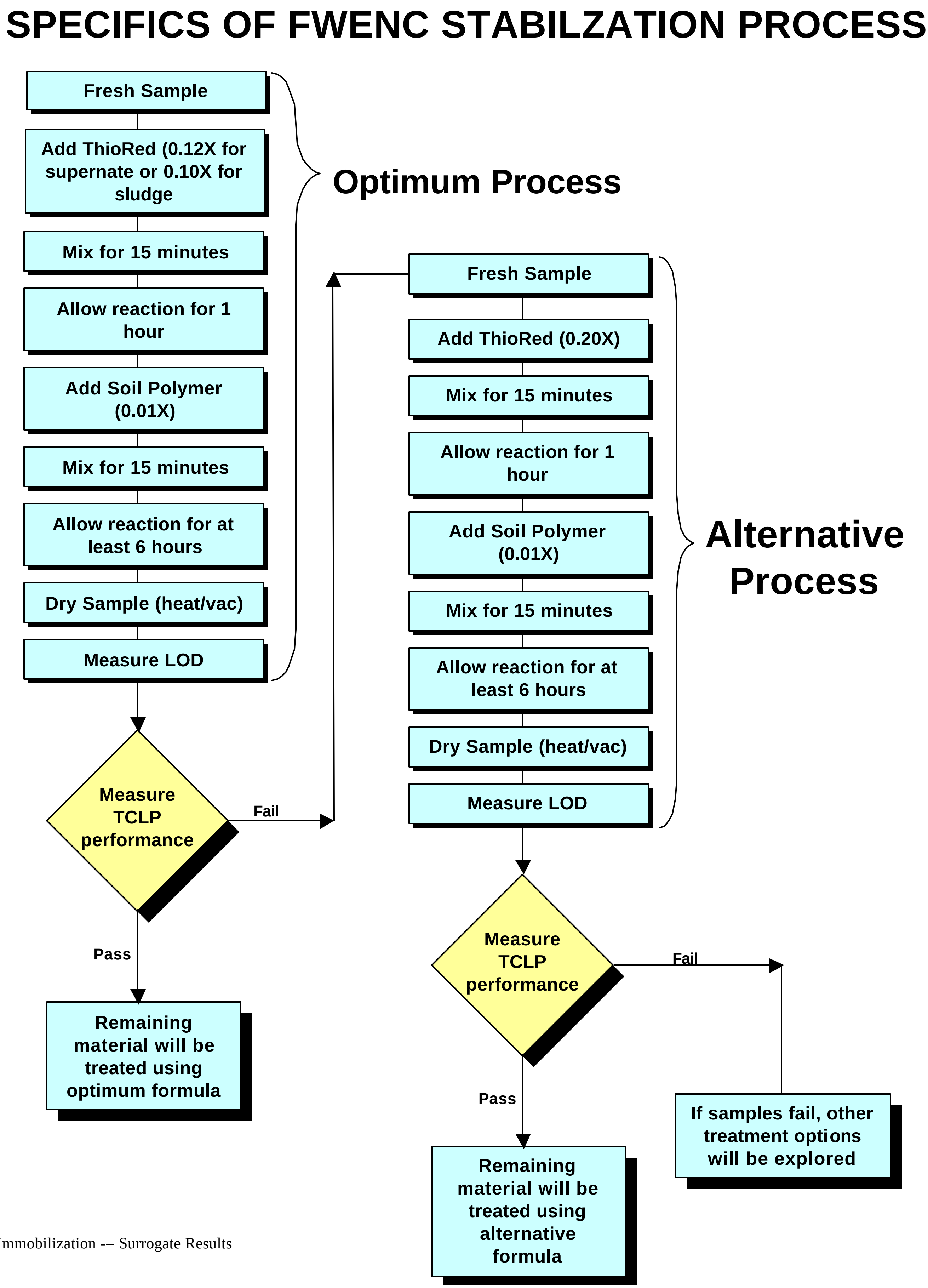


Figure 3. Flowchart of chemical additive processing for the FWENC process.



FIGURES

Figure 4a. Quick and Dirty Surrogate
Figure 4b. QnD during wash/settling
Figure 4c. QnD after 12 hours of settling

Figure 5a. Rinsed QnD sludge after FWENC additives, before drying
Figure 5b. Rinsed QnD sludge after FWENC additives, after drying
Figure 5c. Rinsed QnD sludge after FWENC additives, after drying, top view

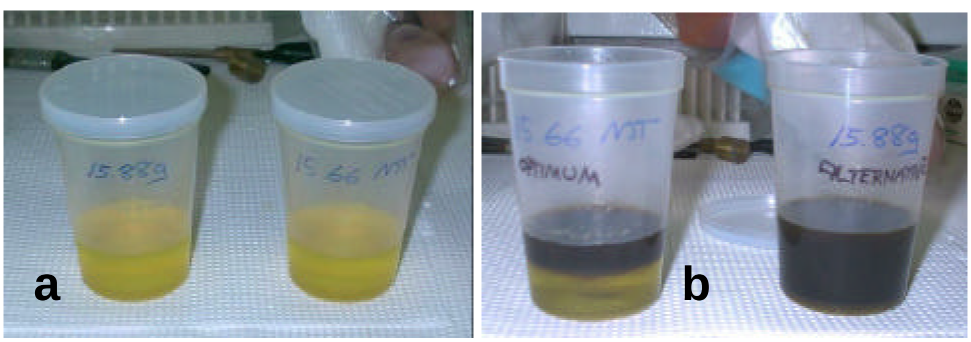


Figure 6a. QnD supernate, untreated
Figure 6b. QnD supernate, after FWENC additive treatment, before drying

Figure 7a. QnD supernate, treated, after drying
Figure 7b. QnD supernate, treated, after drying, top view

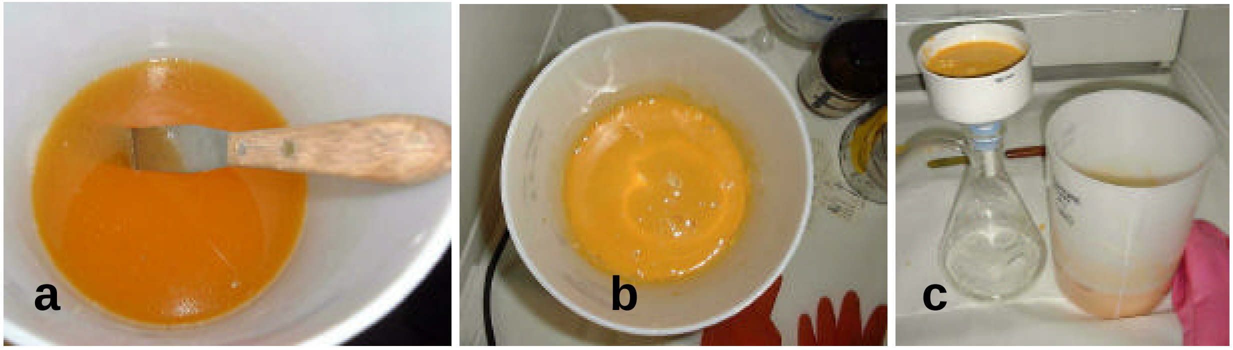


Figure 8a. Preparation of W23S surrogate; mixture before precipitation
Figure 8b. Preparation of W23S surrogate; mixture after precipitation
Figure 8c. Preparation of W23S surrogate; filtration/rinse of precipitant

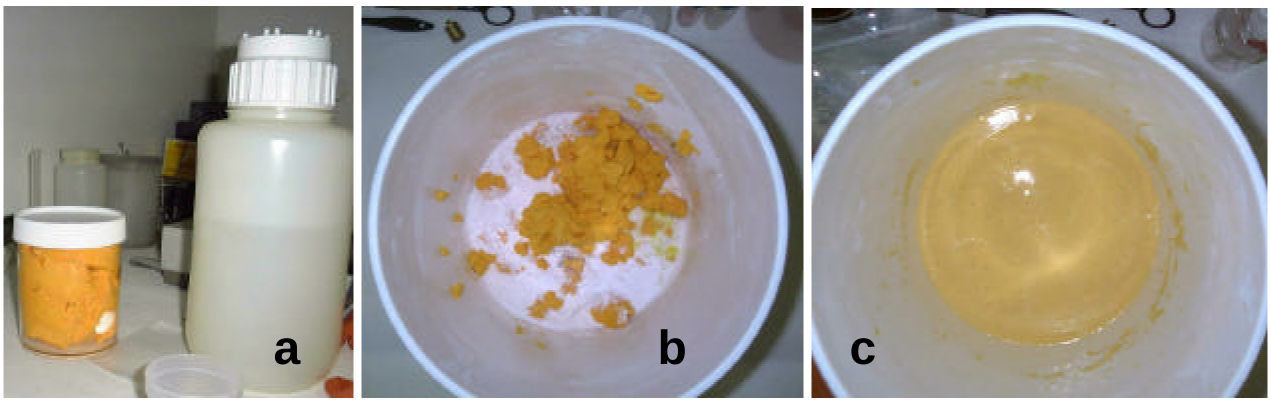


Figure 9a. Preparation of W23S; filter cake and rinse
Figure 9b. Preparation of W23S; addition of chemicals to filter cake
Figure 9c. Final W23S surrogate

Figure 10a. Wash of W23S surrogate
Figure 10b. Sludge from W23S before FWENC treatment
Figure 10c. Treated W23S sludge, before drying

Figure 11a. Treated W23S sludge after drying
Figure 11b. Treated W23S sludge after drying, top view
Figure 11c. Treated W23S sludge, stratification

Figure 12a. Dried MVST Samples (W24, W25, W28) – No Additives
Figure 12b. Close-Up of Dried W24 Sample – No Additives
Figure 12c. Dried W23 and MVST Samples (W23, W26, W27) – Optimum Formula Applied

Figure 13a. Dried MVST W24 Sample – No Additives
Figure 13b. Dried MVST W25 Sample – No Additives
Figure 13c. Dried MVST W28 Sample – No Additives. Note Powdery appearance.

Figure 14a. Dried MVST W23 Sample – Optimum Formula Used. Sample jars also contained a stirring bar, which was added prior to drying to facilitate mixing of FWENC additives.
Figure 14b. Dried MVST W26 Sample – Optimum Formula Used
Figure 14c. Dried MVST W27 Sample – Optimum Formula Used

Appendix A

QnD – Quick and Dirty Surrogate Characterization and Comparison		
Component	Surrogate Concentration (mg/kg surrogate)	W-23 Sample Measured Concentration (mg/kg waste)
Cadmium	51	24
Chromium	352	161
Mercury	76	35
Lead	1,539	705
Aluminum	3,777	1,730
Calcium	124,236	56,900
TIC	14,399	1,320
Iron	3,777	1,730
Potassium	28,166	12,900
Magnesium	23,799	10,900
Sodium	127,074	58,200
Nitrate	174,236	79,800
Nitrite	18,537	8,490
Chlorine	11,397	5,220
Fluorine	1,777	814
Sulfate	19,891	9,110
Strontium	600	275
Thorium	35,808	16,400
Uranium	17,445	7,990
Silicon	4,672	2,140
TOC	6,253	1,550

Appendix B

W23S – Representative Surrogate Characterization and Comparison		
Component	**Surrogate Concentration (mg/kg surrogate)**	**W-23 Sample Measured Concentration (mg/kg waste)**
Cadmium	24	24
Chromium	161	161
Mercury	37	35
Lead	711	705
Aluminum	1729	1730
Calcium	56593	56900
Iron	1754	1730
Sulfate	9170	9110
Potassium	12838	12900
Nitrite	8416	8490
Magnesium	10779	10900
Sodium	58613	58200
Chloride	5151	5220
Fluoride	803	814
Silicon	2134	2140
Strontium	277	275
Nitrate	79143	79800
Thorium	16710	16400
Uranium	8134	7990
TOC	1550	1550

Analysis of Foster Wheeler 'Optimum' Stabilization Process as Applied to W23 and MVST Tank Farm Sludges

John Barton and Roger Spence
October 31, 2000

Summary

Sludges removed from W23 and MVST tank farms were analyzed and subjected to the Foster Wheeler (FWENC) 'Optimum' stabilization process. Three MVST tanks that could pass a wet sludge TCLP prior to treatment also passed after drying, per the FWENC process in the absence of stabilizer additions. In addition, these three tank sludges could now meet UTS criteria (rinsed, wet sludge had previously failed UTS). MVST tank samples from W26 and W27 failed EPA RCRA and UTS criteria for mercury upon TCLP both before and after treatment. W26 and W27 sludges have not yet been subjected to the 'Alternative' stabilization process proposed by FWENC. W23 sludge passed both criteria after 'optimum' treatment. All TCLP/stabilization tests were performed in triplicate to ensure accuracy.

Introduction

During FY2000, representative sludge samples were extracted from six MVST tanks and subjected to a rinsing process prescribed by FWENC that consisted of mixing 1 part sludge with 5 parts water followed by a separation of the settled solids layer (rinsed sludge) from the rinse (rinse supernate). Both the rinsed sludges and rinse supernates (six samples of each) were analyzed for individual metals concentrations with the wet sludges also being subjected to TCLP testing. Of the six sludges that were analyzed, three of the rinsed sludges failed EPA RCRA TCLP limits in mercury: W26, W27, and W31. Of the six rinse supernates, all six failed to meet TCLP requirements in mercury. All failed UTS limits. This report details subsequent processing of these MVST samples, along with sludge samples from W23.

Key Results

Simple Drying of W24, W25, and W28 sludges. Per the FWENC process, the three rinsed sludges that passed a wet TCLP test (EPA RCRA)--from W24, W25, and W28--were vacuum dried and subjected to TCLP testing again. These dried samples all passed EPA RCRA metals limits but did not meet UTS limits in mercury. Wet samples had previously failed UTS limits in both mercury and cadmium. Mercury levels in the TCLP extracts were measured to be (for triplicate, averaged samples) 0.031, 0.037, and 0.053 mg/L for W24, W25, and W28 respectively, which exceed the UTS limit of 0.025 mg/L.

Application of 'Optimum' Process to W26 and W27 Sludges. The two worst-failing tank sludges, W26 and W27, were selected for treatment using the FWENC 'Optimum' process. This required that rinsed sludge samples from both tanks be subjected to a sequence of stabilizer additions followed by vacuum drying. Both of these sludges, even after treatment, continued to fail TCLP limits on mercury.

For Tank W26, the wet TCLP extract level of mercury was measured to be 0.503 mg/L while the dry, treated extract levels (performed in triplicate) were 0.376 ± 0.038, 0.449 ± 0.045, and 0.071 ± 0.007 mg/L. The average of the dry, treated extracts was 0.299 mg/L, which exceeds the EPA RCRA limit of 0.2 mg/L. For W27, the wet TCLP extract level of mercury was measured to be 0.626 mg/L while the dry, treated extract levels (performed in triplicate) were 0.762 ± 0.076, 0.329 ± 0.033, and 0.468 ± 0.047 mg/L. The average of the dry, treated extracts was 0.520 mg/L. In all other metals, both W26 and W26 treated sludge met EPA RCRA and UTS TCLP standards (prior to treatment, W26 sludge had also failed to meet UTS limits for cadmium).

Application of 'Optimum' Process to W23 Sludge. After treatment with the 'Optimum' process (triplicate samples), W23 rinsed sludge pass both EPA RCRA and UTS standards. This result mirrored the work that had been conducted with a representative W23 surrogate.

Additional Information

Requests for additional information regarding the contents of this report or other results from this work should be directed to Mr. Daryl Green at (865) 241-6198 or greendd@oro.doe.gov

Application of FWENC Stabilization Process to Enhance Treated Radioactive Sludge Leach Resistance in Surrogates and Actual Sludges

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Oak Ridge, Tennessee

12th Technical Information Exchange Workshop

Application of FWENC Stabilization Process to Enhance Treated Radioactive Sludge Leach Resistance in Surrogates and Actual Sludges

Roger D. Spence

Chemical Technology Division
Oak Ridge National Laboratory
Oak Ridge, Tennessee

CERS Technical Seminar

Background

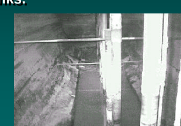
World's first disposal of radioactive waste in Oak Ridge, TN in 1944 – a simple trench filled with unconditioned waste located on the Oak Ridge site.

This photo shows a waste tank being constructed in 1943 in the South Tank Farm at the Oak Ridge Reservation, near Oak Ridge, Tennessee.

Bethel Valley Evaporator Service Tank (BVEST W23)

- Installed in the 1960s and 1970s, the tanks are 12 feet in diameter and 61.5 feet long
- They store evaporator concentrate and dilute radioactive liquid low level waste
- Precipitants from the cooled evaporator waste have formed a sludge layer 3 to 5 feet deep in the tanks.

BVEST Site



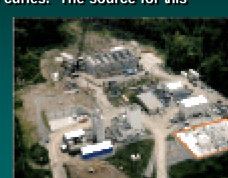
Inside W-21

Project History

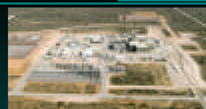
- Project arose in response to DOE concerns that a private vendor's (Foster Wheeler Environmental Corporation – FWENC) proposed MVST waste stabilization process might fail leach requirements
- Initiated in FY 2000
- Collaborative effort between EM30 and EM50's Tanks Focus Area

Melton Valley Storage Tanks (MVST)

The eight Melton Valley Storage Tanks (MVST) at the Oak Ridge Reservation are 50,000 gallon horizontal stainless steel "cigar" tanks. They have a primary shell which holds the waste and a secondary shell that stops leaked waste before it can reach the environment. The tanks contain 200,000 gallons of supernate with 20,000 curies and 100,000 gallons of sludge with 100,000 curies. The source for this waste is residuals from gunite tanks and newly generated waste from reactors and decontamination and decommissioning operations. The supernates are classified as mixed low-level waste. The sludges are mixed transuranic waste. Six new 100,000 gal tanks are being built in the Melton Valley area.



Waste Isolation Pilot Plant



- The Waste Isolation Pilot Plant, or WIPP, is the world's first underground repository licensed to safely and permanently dispose of transuranic radioactive waste left from the research and production of nuclear weapons. After more than 20 years of scientific study, public input, and regulatory struggles, WIPP began operations on March 26, 1999.
- Located in the remote Chihuahuan Desert of Southeastern New Mexico, project facilities include disposal rooms mined 2,150 feet underground in a 2,000-foot thick salt formation that has been stable for more than 200 million years. Transuranic waste is currently stored at 23 locations nationwide. Over the next 35 years, WIPP is expected to receive about 37,000 shipments.

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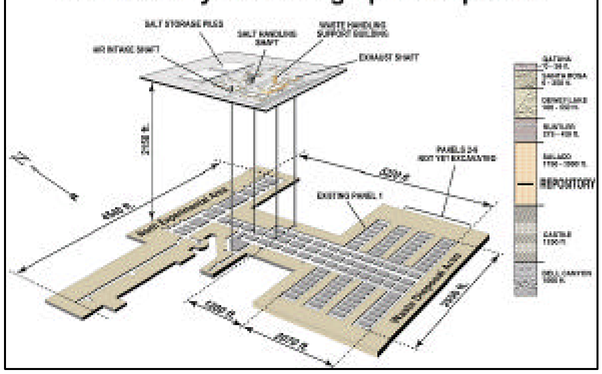
WIPP Facility and Stratigraphic Sequence



Nevada Test Site

The Waste Management Program disposal facilities at the Nevada Test Site accept both on-site and off-site low-level waste for disposal

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Project Goals

- To evaluate the approach taken by the private vendor, Foster Wheeler for immobilization of OR tank waste
- Evaluation includes both immediate and longer-term leach testing to ensure that the tank waste forms retain hazardous metals and meet RCRA TCLP limits
- Results of testing with both actual and simulated waste streams compared

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Outline

- The Foster Wheeler Process
- Description of Surrogate Work
- Initial Surrogate Results
- Description of work with W23 and MVST Actual Waste
- Initial Stabilization Results
- Ongoing and future long term stabilization studies

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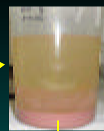
"Quick & Dirty" Surrogate

12 hrs settling



- Preparation and stabilization of a traditional surrogate tank waste for quick turnaround
- Simple mixing of RCRA, process, and radionuclide metals together to generate a rough simulation of the composition of tank wastes

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"Quick & Dirty" Surrogate Composition

[illegible] - Quick and Dirty Surrogate Characterization and Comparison		
Component	Surrogate Concentration (mg/kg surrogate)	W23 Sample Measured Concentration (mg/kg waste)
Cadmium	51	34
Chromium	312	101
Mercury	70	85
Lead	1,509	705
Aluminum	3,777	1,738
Calcium	124,236	56,900
TIC	14,959	1,528
Iron	3,777	1,738
Potassium	28,168	12,800
Magnesium	23,798	10,800
Sodium	127,074	58,200
Nitrate	174,235	79,800
Nitrite	18,533	8,488
Chlorine	11,397	5,220
Fluorine	1,777	814
Sulfate	13,991	6,119
Strontium	680	375
Thorium	35,808	16,400
Uranium	17,445	7,990
Silicon	4,672	2,140
TOC	8,258	1,558

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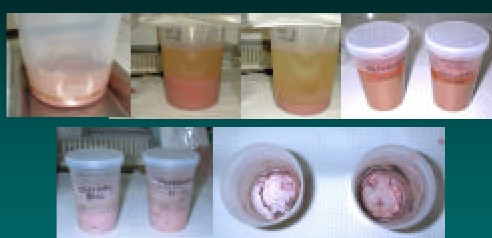
Start to Finished QnD Waste Form



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Stabilization of Surrogate Rinse

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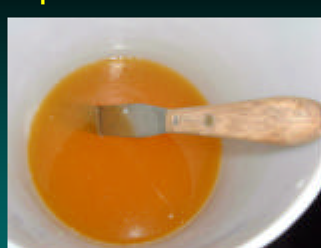
W23 Surrogate Preparation

Preparation of a surrogate highly representative of W23 tank wastes--RCRA metals, radionuclides, & bulk components must be present in the right concentrations



Mixing soluble chemicals—nitrates, chlorides

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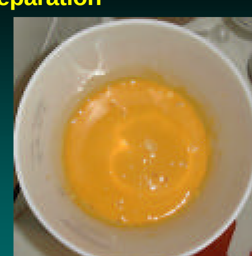
W23 Surrogate Preparation

Preparation of a surrogate highly representative of W23 tank wastes--RCRA metals, radionuclides, & bulk components must be present in the right concentrations



Precipitation using hydroxide

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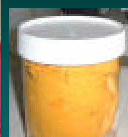
W23 Surrogate Preparation

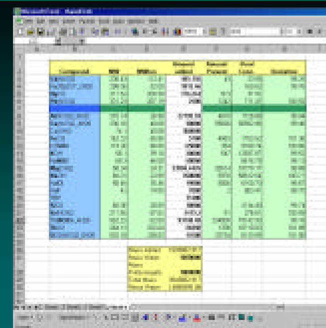
Preparation of a surrogate highly representative of W23 tank wastes--RCRA metals, radionuclides, & bulk components must be present in the right concentrations



Rinsing of resulting solids with DI water to remove soluble components

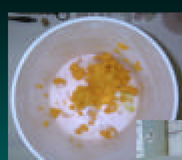
W23 Surrogate Preparation

By analyzing filter cake, small amounts of additional material needed to make the surrogate highly representative can be determined



W23 Surrogate Preparation

Preparation of a surrogate highly representative of W23 tank wastes--RCRA metals, radionuclides, & bulk components must be present in the right concentrations



Adding rinsed sludge to new components

Final Representative Surrogate

W23 Representative Surrogate Composition

W23 – Representative Surrogate Characterization and Comparison

Component	Surrogate Concentration (mg/kg surrogate)	W-23 Sample Measured Concentration (mg/kg waste)
Cadmium	24	24
Chromium	161	161
Mercury	37	35
Lead	711	706
Aluminum	1720	1738
Calcium	58583	58080
Iron	1764	1738
Sulfate	8170	9118
Potassium	12086	12080
Nitrite	8436	9498
Magnesium	16779	18980
Sodium	69913	68280
Chloride	8181	8228
Fluoride	803	814
Silicon	3134	2148
Strontium	377	376
Nitrate	78143	78080
Thorium	16710	18480
Uranium	8134	7998
TOC	1550	1858

Start to Finished W23 Surrogate Waste Form

What determines whether a waste form has been stabilized?

- Toxic Characteristic Leaching Procedure analyses are performed on a sample extract which is prepared in a manner to simulate the climatic leaching action expected to occur in landfills. A solid sample is extracted with one of the appropriate aqueous extraction (leaching) solutions described in the EPA test method.
- Analyses for specific metals, volatile organics, semivolatile organics, pesticides, and herbicides are performed on the leachate. If the concentration of any of the specified compounds is found to be present in the leachate above the regulatory level, the waste is a CHARACTERISTIC WASTE and must carry a "D" code.

What determines whether a waste form has been stabilized?

- LDR Universal Treatment Standards (UTS) are much more stringent limits which EPA is promoting.

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RCRA versus UTS LDRs

Component	EPA Characteristic Limit Concentration (mg/L)	UTS (mg/L)
Cadmium	1.0	0.11
Chromium	5.0	0.6
Mercury	0.2	0.025
Lead	5.0	0.75
Uranium	Not applicable	Not applicable
Thorium	Not applicable	Not applicable

Examples of the more stringent nature of the UTS limits

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Quick and Dirty Sludge TCLP Pre- and Post-Treatment

No Treatment

Component	Measured Concentration (mg/L)	EPA Characteristic Limit Concentration (mg/L)
Cadmium	0.001	1.0
Chromium	11.69	5.0
Mercury	1.123	0.2
Lead	12.91	5.0
Uranium	0.083	Not applicable
Thorium	<0.500	Not applicable

After Optimum Treatment

Component	Measured Concentration (mg/L)	EPA Characteristic Limit Concentration (mg/L)
Cadmium	<0.002	1.0
Chromium	0.539	5.0
Mercury	0.000091	0.2
Lead	0.862	5.0
Uranium	5.50	Not applicable
Thorium	1.67	Not applicable

ORNL CERS/TFA/009

Quick and Dirty Surrogate Rinse TCLP Pre- and Post-Treatment

No Treatment

Component	Calculated TCLP Leach Concentration (mg/L) based on tank analysis	EPA Characteristic Limit Concentration (mg/L)
Cadmium	<0.002	1.0
Chromium	28.48	5.0
Mercury	1.522	0.2
Lead	26.50	5.0
Uranium	9.19	Not applicable
Thorium	<0.500	Not applicable

After Optimum Treatment

Component	Measured Concentration (mg/L)	EPA Characteristic Limit Concentration (mg/L)
Cadmium	0.009	1.0
Chromium	0.194	5.0
Mercury	0.000968	0.2
Lead	1.154	5.0
Uranium	0.409	Not applicable
Thorium	<0.500	Not applicable

ORNL CERS/TFA/009

W23 Surrogate Sludge TCLP Pre- and Post-Treatment

No Treatment

Component	Measured Concentration (mg/L)	EPA Characteristic Limit Concentration (mg/L)
Cadmium	0.0059	1.0
Chromium	17.524	5.0
Mercury	1.785	0.2
Lead	13.53	5.0
Uranium	1.14	Not applicable
Thorium	1.662	Not applicable

After Optimum Treatment

Component	Measured Concentration (mg/L)	EPA Characteristic Limit Concentration (mg/L)
Cadmium	0.005	1.0
Chromium	0.379	5.0
Mercury	0.000702	0.2
Lead	0.861	5.0
Uranium	0.248	Not applicable
Thorium	0.222	Not applicable

ORNL CERS/TFA/009

W23 Surrogate Rinse TCLP Pre- and Post-Treatment

No Treatment

Component	Measured Concentration (mg/L)	EPA Characteristic Limit Concentration (mg/L)
Cadmium	<0.002	1.0
Chromium	24.026	5.0
Mercury	1.510	0.2
Lead	13.672	5.0
Uranium	2.473	Not applicable
Thorium	<0.500	Not applicable

After Optimum Treatment

Component	Measured Concentration (mg/L)	EPA Characteristic Limit Concentration (mg/L)
Cadmium	<0.002	1.0
Chromium	0.367	5.0
Mercury	0.267	0.2
Lead	0.284	5.0
Uranium	1.51	Not applicable
Thorium	1.41	Not applicable

ORNL CERS/TFA/009

Surrogate Results for EPA RCRA Limits

- Both the sludge and rinse (supernate) from both surrogates fail to pass TCLP requirements without treatment
- Both sludges passed after receiving the 'Optimum treatment
- The representative W23 rinse/supernate failed regardless of treatment method

	Wet TCLP/Analysis	Dried Waste Form (no additives)	Optimum Treatment	Alternative Treatment
QnD Sludge	Fail	Not Tested	Pass	Pass
QnD Supernate	Fail	Not Tested	Pass	Pass
W23S Sludge	Fail	Fail	Pass	Pass
W23S Supernate	Fail	Not Tested	Fail	Fail

Surrogate Results for UTS Limits

- The stabilization technique proposed by FWENC failed to impact any of the UTS limits

	Wet TCLP/Analysis	Dried Waste Form (no additives)	Optimum Treatment	Alternative Treatment
QnD Sludge	Fail (Pb, Cr, Hg)	Not Tested	Fail (Pb)	Fail (Pb, Cr)
QnD Supernate	Fail (Pb, Cr, Hg)	Not Tested	Fail (Pb)	Fail (Pb)
W23S Sludge	Fail (Pb, Cr, Hg)	Fail (Pb, Cr, Hg)	Fail (Pb)	Fail (Pb)
W23S Supernate	Fail (Pb, Cr, Hg)	Not Tested	Fail (Hg)	Fail (Hg)

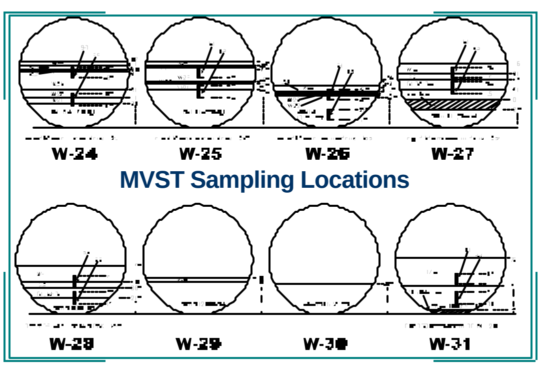
Actual Tank Wastes

We were also tasked with examining this process on actual tank wastes from MVST and BVEST W23

BVEST W23

- W23 passes RCRA TCLP limits without treatment, but fails UTS in cadmium and mercury
- 'Optimum' treatment reduces leach concentrations of metal bad actors
- Treated sludge fails UTS limits on cadmium (0.11 mg/L)

Component	TCLP Concentration Before Treatment (mg/L)	TCLP Concentration After Treatment (mg/L)
Cadmium	0.746	0.222
Chromium	0.563	0.081
Mercury	0.0337	< 0.008, nondetect
Lead	0.68[illegible]	0.393



Actual Tank Wastes After Treatment

MVST Tank Waste TCLP Results (EPA RCRA Std)

No Treatment

MVST Tank	Wet TCLP	Supernate-wash
W-24	Pass	Fail
W-25	Pass	Fail
W-26	Fail	Fail
W-27	Fail	Fail
W-28	Pass	Fail
W-31	Fail	Fail

After Optimum Treatment

W-24 (drying only)	Pass	Not Measured
W-25 (drying only)	Pass	Not Measured
W-26 (Optimum treatment)	Fail	Not Measured
W-27 (Optimum treatment)	Fail	Not Measured
W-28 (drying only)	Pass	Not Measured
W-31	Not measured	Not Measured

ORNL CERS/TFA/009

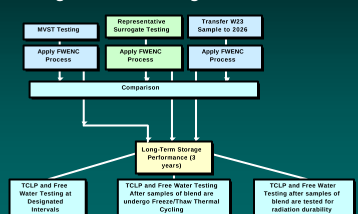
Future and Ongoing Work

- Apply FWENC 'Alternative' Treatment to actual tank wastes
- Apply FWENC Process to Tank Sludge Rinse (Supernate)
- Long Term Testing of Surrogate and Actual Tank Sludge

ORNL CERS/TFA/009

Long Term Testing

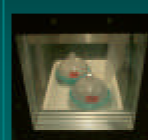
- TCLP and Free Water Testing at Designated Intervals
- Radiation Testing
- Thermal Degradation Testing



ORNL CERS/TFA/009

Freeze-Thaw Testing of Surrogate Sludge

- -40 °C to 60°C
- 30 Cycles
- 30 min temperature ramp
- 3 hour hold time
- Saturated salt solutions used to control humidity



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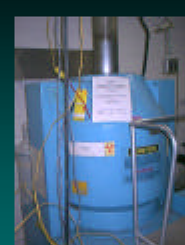
Long Term Testing of Surrogate Sludge Under Ambient Conditions

- Unconditioned section of trailer, subject to natural extremes of temperature and humidity
- Located on OR Site

ORNL CERS/TFA/009

Radiation Durability Testing

- Cobalt Source (10^5 rad/hr) to be used
- Samples subjected to 10^8 rads, which is the recommended maximum activity level for waste forms that contain organic media [10 CFR 61.56(b)(1)]
- Dose of radiation is approximately equivalent to the dose that would be acquired by a waste form over a 300-year period, if the waste form were loaded to a Cesium-137 or Strontium-90 concentration of 10 Ci/ft^3

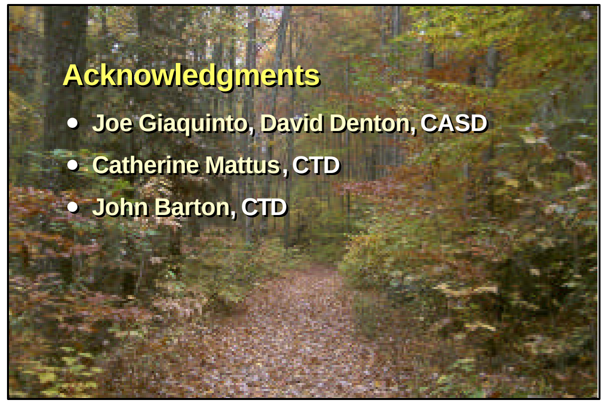


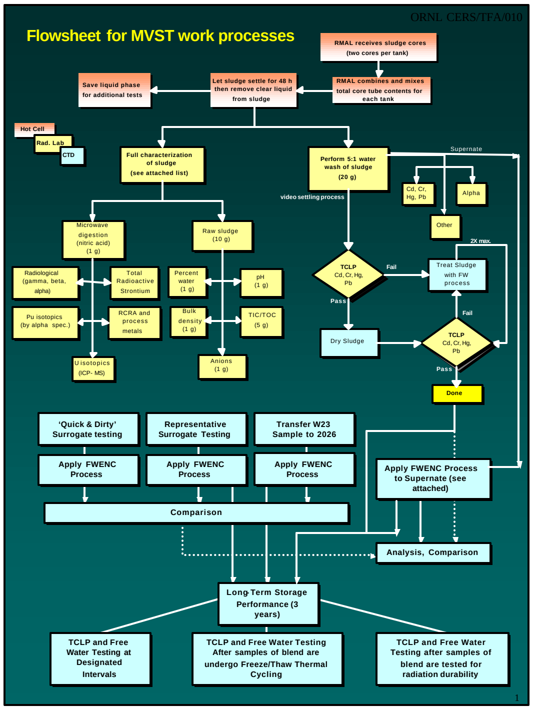
ORNL CERS/TFA/009

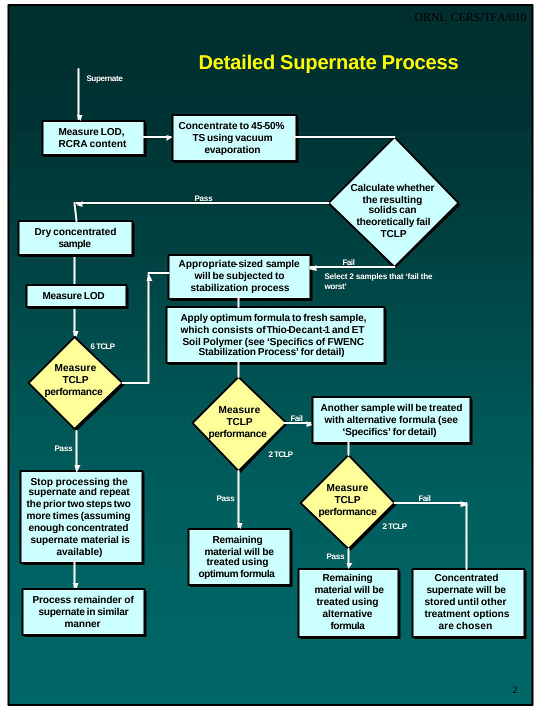
Summary

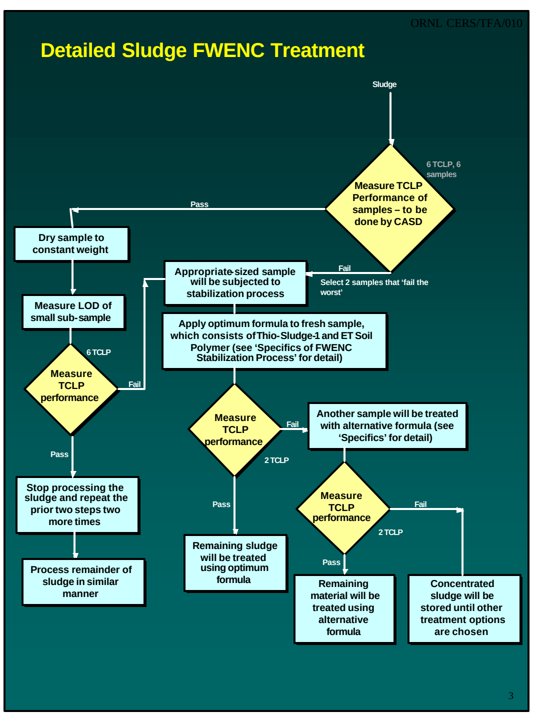
- FWENC 'Optimum' process stabilizes both surrogate sludges, but fails to stabilize the rinse from the more representative surrogate
- FWENC 'Optimum' process stabilizes BVEST W23 tank sludge to RCRA standard
- FWENC 'Optimum' process fails to stabilize MVST Tank sludges in mercury
- The process will not meet UTS limits for either surrogates or actual tank wastes

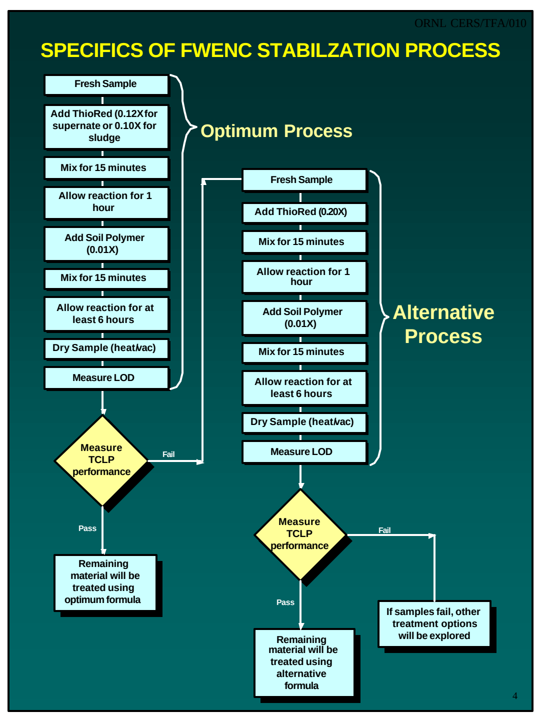
ORNL CERS/TFA/009




ORNL CERS/TFA/010
Flowsheet for MVST work processes
RMAL receives sludge cores (two cores per tank)
RMAL combines and mixes total core tube contents for each tank
Let sludge settle for 48 h then remove clear liquid from sludge
Save liquid phase for additional tests
Hot Cell
Rad. Lab
CTD
Full characterization of sludge (see attached list)
Perform 5:1 water wash of sludge (20 g)
Supernate
Cd, Cr, Hg, Pb
Alpha
Other
video settling process
Microwave digestion (nitric acid) (1 g)
Raw sludge (10 g)
Radiological (gamma, beta, alpha)
Total Radioactive Strontium
Percent water (1 g)
pH (1 g)
Pu isotopics (by alpha spec.)
RCRA and process metals
Bulk density (1 g)
TIC/TOC (5 g)
U isotopics (ICP- MS)
Anions (1 g)
TCLP Cd, Cr, Hg, Pb
Fail
Treat Sludge with FW process
2X max.
Pass
Dry Sludge
Fail
TCLP Cd, Cr, Hg, Pb
Pass
Done
'Quick & Dirty' Surrogate testing
Representative Surrogate Testing
Transfer W23 Sample to 2026
Apply FWENC Process
Apply FWENC Process
Apply FWENC Process
Apply FWENC Process to Supernate (see attached)
Comparison
Analysis, Comparison
Long-Term Storage Performance (3 years)
TCLP and Free Water Testing at Designated Intervals
TCLP and Free Water Testing After samples of blend are undergo Freeze/Thaw Thermal Cycling
TCLP and Free Water Testing after samples of blend are tested for radiation durability
1


ORNL CERS/TFA/010
Detailed Supernate Process
Supernate
Measure LOD, RCRA content
Concentrate to 45-50% TS using vacuum evaporation
Calculate whether the resulting solids can theoretically fail TCLP
Pass
Dry concentrated sample
Fail
Appropriate-sized sample will be subjected to stabilization process
Select 2 samples that 'fail the worst'
Measure LOD
Apply optimum formula to fresh sample, which consists of Thio-Decant-1 and ET Soil Polymer (see 'Specifics of FWENC Stabilization Process' for detail)
6 TCLP
Measure TCLP performance
Measure TCLP performance
Fail
Another sample will be treated with alternative formula (see 'Specifics' for detail)
2 TCLP
Pass
Pass
Stop processing the supernate and repeat the prior two steps two more times (assuming enough concentrated supernate material is available)
Remaining material will be treated using optimum formula
Measure TCLP performance
Fail
2 TCLP
Pass
Remaining material will be treated using alternative formula
Concentrated supernate will be stored until other treatment options are chosen
Process remainder of supernate in similar manner
2


ORNL CERS/TFA/010
Detailed Sludge FWENC Treatment
Sludge
6 TCLP, 6 samples
Measure TCLP Performance of samples – to be done by CASD
Pass
Dry sample to constant weight
Fail
Appropriate-sized sample will be subjected to stabilization process
Select 2 samples that 'fail the worst'
Measure LOD of small sub-sample
Apply optimum formula to fresh sample, which consists of Thio-Sludge-1 and ET Soil Polymer (see 'Specifics of FWENC Stabilization Process' for detail)
6 TCLP
Measure TCLP performance
Fail
Measure TCLP performance
Fail
Another sample will be treated with alternative formula (see 'Specifics' for detail)
2 TCLP
Pass
Pass
Measure TCLP performance
Fail
2 TCLP
Stop processing the sludge and repeat the prior two steps two more times
Remaining sludge will be treated using optimum formula
Pass
Remaining material will be treated using alternative formula
Concentrated sludge will be stored until other treatment options are chosen
Process remainder of sludge in similar manner
3


ORNL CERS/TFA/010
SPECIFICS OF FWENC STABILZATION PROCESS
Fresh Sample
Add ThioRed (0.12X for supernate or 0.10X for sludge
Optimum Process
Mix for 15 minutes
Allow reaction for 1 hour
Add Soil Polymer (0.01X)
Mix for 15 minutes
Allow reaction for at least 6 hours
Dry Sample (heat/vac)
Measure LOD
Fresh Sample
Add ThioRed (0.20X)
Mix for 15 minutes
Allow reaction for 1 hour
Add Soil Polymer (0.01X)
Mix for 15 minutes
Allow reaction for at least 6 hours
Dry Sample (heat/vac)
Measure LOD
Alternative Process
Measure TCLP performance
Fail
Pass
Remaining material will be treated using optimum formula
Measure TCLP performance
Fail
Pass
If samples fail, other treatment options will be explored
Remaining material will be treated using alternative formula
4

ORNL CERS/TFA/012

OAK RIDGE NATIONAL LABORATORY

MANAGED BY UT-BATTELLE FOR THE DEPARTMENT OF ENERGY

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January 12, 2001

Ms. Jacquie Noble-Dial, Jr.
Field Office Site Representative
Department Of Energy - Oak Ridge
P.O. Box 2001, EM-93
Oak Ridge, TN 37831

Dear Ms. Noble-Dial, Jr.:

This cover letter is written to introduce, for your review, the enclosed Meeting Report for the TFA Review Meeting held at Oak Ridge National Laboratory on January 9, 2001 for OR0-0-WT-31, 3TKH, Technical Response 99019, ORNL Immobilization (PI: Roger Spence).

The meeting report includes various notes/comments from the meeting, some further analysis based upon those notes, and a revised test plan for future FY01 work.

With your approval and review for changes, I will be happy to help you distribute this document to the appropriate parties.

For additional information, please contact myself (865-241-5706) or Roger Spence (865-574-6782).

Sincerely,

JWBarton

J. W. Barton
Staff Engineer, Chemical Technology Division
ORNL

Enclosure

cc: J. Harbour (SRS)
B. Holtzscheiter (SRS)
C. Langton (SRS)
L. Klatt (ORNL)
C. Langton (SRS
R. Spence (ORNL)

ORNL IMMOBILIZATION:
TFA Review Meeting

OR00WT31, 3TKH

John Barton
Roger Spence

January 12, 2001

Meeting Date

January 9, 2001 at Oak Ridge National Laboratory, Oak Ridge, TN

Summary

TFA representatives met with EM-30 and EM-50 program managers, the ORNL project PI and engineers, Foster Wheeler Environmental Corporation (FWENC) representatives, and representatives from Bechtel Jacobs managing Melton Valley Storage Tank (MVST) operations to discuss recent results from OR00WT31, 3TKH, ORNL Immobilization. This project provides an independent review of a proposed process for stabilizing MVST sludges and supernates (supported by EM-30 under a contract to FWENC). Both surrogate and actual tank sludge data collected suggest that the FWENC process for tank stabilization may not work on all of the various MVST tanks. A test plan, presented below, was developed based on these initial results and will be implemented during FY01.

The Foster Wheeler Process

The process to be applied by FWENC to stabilize MVST sludges involves mixing the sludge with water in a 1:5 volume ratio. After 12 hours, the rinse is separated from the settled sludge and added to existing tank liquids. Both the sludge and supernate portions generated are to be stabilized by addition of two commercially available stabilizing agents to the portions, followed by drying process that reduces the volume of each waste portion. For further details of the FWENC process, see ORNL Report CERS/TFA/001.

Stabilizing Agents. The chemical additives which are used to stabilize RCRA metals in the sludge are commercially available from Etus, Inc. (Sanford, Fl). The first stabilizer added, Thio-Red™, is a reddish-brown liquid that contains proprietary amounts/species of thiocarbonate. Upon addition of Thio-Red, dark, fluffy, buoyant flocs form. This is suspected to be mercuric sulfide, although ETUS literature indicates that this agent generates stable metal thiocarbonates. Some additional information on Thios-Red™ is available in

Henke, KR, "Chemistry of Heavy Metal Precipitates Resulting From Reactions With Thio-Red," *Water Environment Research*, 70, 1178-85 (1998).

The second additive is called 'ET Soil Polymer', and is an alkali silicate. Physically it is a hygroscopic, white powder. According to the Material Safety Data Sheet provided by Etus, Inc., this additive should be completely soluble in water.

Surrogate Results

Results from the Foster Wheeler process were described as applied to two different surrogates. The first surrogate, which was prepared by simple mixing of reagent grade chemicals in appropriate proportions to roughly simulate actual tank wastes, was stabilized by the 'Optimum' FWENC process in terms of both the rinsed sludge and the rinse water generated by the process. The second surrogate was designed to be more representative of Bethel Valley Evaporation Storage Tank (BVEST) W23 tank waste, from which we had actual tank samples on hand and immediately available for testing. The procedure used to create this surrogate involved proportioned mixing of soluble components, followed by a hydroxide precipitation, soluble species filtration and rinsing, and then a chemical species tweaking via analysis and addition of missing components. When the FWENC process was applied to this surrogate, the sludge portion generated was stabilized by the FWENC 'Optimum' process, whereas the rinse waters were not stabilized by either the 'Optimum' or 'Alternative' processes. This surrogate deviated by less than 2% in elemental/complex anion composition of more than 20 of the key species analyzed in W23 actual sludge. Speciation differences between surrogate and actual tanks are likely however, primarily since no speciation data exist for any of the MVST tanks to enable preparation of a better surrogate. We chose to use the most soluble species as a conservative approach.

Data Scatter. The 'Optimum' FWENC process failed (in mercury leach only) to stabilize the rinse water in only one of the triplicate runs; the average for the triplicate tests failed to pass as well. The 'Alternative' FWENC process as applied to the rinse did not provide any enhancement; triplicate runs all indicated failure in mercury leach. These tests will be repeated for better accuracy and precision.

All RCRA and process metal species, including thorium and uranium, were analyzed before and after treatment.

Process notes from surrogate work. As noted above, Thio-Red addition caused a dark, fluffy, buoyant floc to appear instantly (this was most apparent in the rinse-stabilization tests). ET Soil Polymer, when added, appeared to sink (without vigorous stirring) and *did not* appear to dissolve as claimed in the Material Safety Data Sheets provided by the supplier.

The end product of surrogate sludge stabilization was a chalky, stratified 'cake'. During the drying process, some salts precipitated before others, which created a visible 'layered' effect. Presumptively, a layer of mercury sulfide formed on the top of each cake (dark, black layer). Rinse water stabilization resulted in a much more crystalline solid. During the evaporation process (prior to stabilizer addition), some crystallization was noted. This may have prevented the additives from effectively stabilizing all of the supernate components. Drying for both surrogate sludge and rinse required several days and seems to be inefficient. The FWENC protocol requires test samples to be dried at 80^{o}C under 20"Hg pressure (low vacuum)—because convective drying/moisture removal is minimized under these conditions, drying rates were low.

Some 'spatter' was noted during drying of the sludge component, as bubbles of gas were released from the internal structure of the sludge after the exterior portions had hardened. This phenomenon is thought to make the end sludge product more porous.

Significant volume reduction in both rinse (~90%) and sludge (> 70%) were noted after drying.

Long term testing. Freeze-thaw long-term testing of one surrogate has been completed. These experiments involved subjecting stabilized sludge samples to cycled extremes of temperature (-40^{o}C to 60^{o}C, 30 cycles) over a period of one week under two different relative humidity conditions (35% and 85% RH). In all triplicate runs, the surrogate remained stable. Although some hydration occurred, no visible free water accumulated.

Radiation durability testing (Nuclear Regulatory Guidelines are being used) of stabilized sludge will be completed this FY. This effort will continue but may not directly impact waste acceptance criteria associated with the eventual disposal sites for EM-30 MVST work. The information will be used to provide a better understanding of stability of Thio-Red (an organic) under high radiation conditions.

Stabilized surrogate sludge samples have also been placed in an unconditioned trailer for exposure tests to extremes of heat and humidity typical of upper east Tennessee. Visible free water and RCRA stabilization will be examined at periodic intervals.

W23 Stabilization

W23 tank sludges were subjected to the FWENC 'Optimum' process and were successfully stabilized. It must be noted that earlier work with W23 had shown that this sludge would pass TCLP even without the treatment. The 'Optimum' process did impact the mercury leach concentrations substantially, bringing them below detection limits--without 'Optimum' treatment, levels were measured to be 0.034 ppm in 'wet' TCLP tests; after treatment and drying, the levels were below 0.008 ppm. The mercury concentration in W23 was measured to be approximately 35 ppm, which is lower than the average measured concentrations of mercury for MVST tank sludges (82 ppm).

Comparison to surrogate. Elemental analysis shows that the surrogate is very close in composition to actual W23 tank samples, although speciation differences are likely. One key difference between the W23 sludge and the precipitated surrogate was that the surrogate failed TCLP testing in three RCRA metals unless the 'Optimum' process was applied, thus making the surrogate more conservative. Again, this is likely due to speciation differences between the two mixtures. Supernate comparisons cannot yet be drawn.

MVST Stabilization

Sludge samples from six of the MVST tanks (W24, W25, W26, W27, W28, and W31) were obtained during FY00 and submitted for 'wet' TCLP analysis. Two of these sludges (W26, W27) failed TCLP in mercury without any further treatment. W31 passed by a close margin (0.195 ppm) and should also receive stabilizing additive treatment.

Even though some of the tanks passed the ‘wet TCLP tests, the FWENC protocols require that ‘passing’ sludges be dried under the same drying conditions and re-tested for stability. This procedure was completed on W24, W25, and W28 sludge samples with all samples passing TCLP requirements. Each drying treatment was run in triplicate, with good precision between runs.

Based on earlier meetings with EM-30 and FWENC representatives, the two failing tank sludges from W26 and W27 were subjected to the ‘Optimum’ process in triplicate. Both sludges failed to passed after this treatment, with good agreement between triplicate runs. Individual mercury leach concentrations, as well as other data, may be found in the presentation slides referenced in the Summary.

In general, the FWENC ‘Optimum’ process does not appear to stabilize mercury levels in tank sludges. The ‘Alternative’ process has not been applied and tested. ‘Alternative’ tests will not be performed until later decision points are reached regarding the rinse waters.

Comparison with surrogate. The results obtained for W24, W25, and W28 were all very similar to the results obtained from the precipitated W23 surrogate, perhaps since the mercury levels of those three MVST tanks (average of 58 ppm) were closer to the surrogate (35 ppm) than the other tanks tested (W26 and W27, which had an average mercury content of 127 ppm).

Process notes from actual ‘hot’ tank work. Sludges which were dried and/or treated using the FWENC process did not visibly stratify during the drying procedure. Extreme spattering was noted during drying, which was related again to water vapor expanding within central portions of the sludge. Drying of the sludges required several days under the prescribed conditions. Filtered TCLP solutions from these tests were clear, indicating an efficient separation of undissolved solids during the EPA protocol. Some frothing during handling was noted, indicating high ionic or surfactant activity.

Document Control

Prior reports have now been assigned control numbers and are currently being cleared for public released. When all reports have been officially cleared, we will make these documents available by weblinks to interested parties.

The Bayne Report

Foster-Wheeler representatives indicated at this meeting that mercury levels in the MVST tank supernates were low enough such that treatment would not be necessary. It was not clear whether FWENC had actually performed those analyses independently, but FWENC stated that data in the Bayne Report support this claim. A reference for the Bayne report, and its Addendum, is as follows:

CK Bayne, JR DeVore, & AB Walker. *Statistical Description of Liquid Low-Level Waste System Supernatant Liquids At Oak Ridge National Laboratory*. ORNL/TM-13351 and ORNL/TM13351 Addendum 1. Oak Ridge National Laboratory, Oak Ridge, Tennessee. October, 1997.

The Bayne Report contains historic data for several waste tanks at ORR, including the MVST tanks, up to 1996. The Addendum in particular addresses physical and chemical characteristics of the liquid supernatants. Because the MVSTs are part of an active waste system, the report indicates that the values examined vary widely from year to year. Discussions with one of the report's authors (AB Walker) indicated that current tank supernatant concentrations are likely to be very different from numbers reported in the Report, and potentially much higher due to concentration efforts. Also, 'unlike the sludge, the supernatants in all tanks were produced from the same processes, were treated by the same evaporation process, and have been mixed between some tanks freely.'

By selecting the most recent (1996) data for the supernatants, which may be highly inaccurate, Table I was generated for the MVST supernatants present at that time, indicating supernatant mercury levels and their potential leachability:

Table I. Based on 1996 measurements of MVST supernatants (Bayne et al, 1997), all but one of the MVST supernatants would pass TCLP. The RCRA leach limit on mercury is 0.2 ppm.

MVST Tank	Mercury Concentration in Actual Supernate (ppm)	Total Solids Measurement (ppm)	Theoretical TCLP Mercury Leach Concentration (ppm)
W24	0.1	320	**0.016**
W25	0.1	360	**0.014**
W26	0.9	430	**0.105**
W27	0.3	390	**0.038**
W28	0.2	580	**0.017**
W31	2.3	440	**0.261**

When considering the rinse water from the sludge treatment process (a 5:1 volume ratio of added water) as applied to samples we received during FY00, analytical results yielded the results shown in Table II. This analysis assumes a good separation of solids from supernate during the rinse process; Bayne results have shown that Total Dissolved Solids are very close to the Total Solids Measurement for supernate.

Table II. Data collected from rinses of the MVST sludges (collected in 2000) indicate that at least three of the tanks (W26, W27, and W31) could fail. The remaining tanks were close to failure. The RCRA leach limit on mercury is 0.2 ppm.

MVST Tank	Mercury Concentration in Supernate (ppm)	Total Dissolved Solids Measurement (ppm)	Theoretical TCLP Mercury Leach Concentration (ppm)
W24	0.302	107	**0.141**
W25	0.220	124	**0.089**
W26	2.750	154	**0.893**
W27	2.090	41.4	**2.524**
W28	0.307	117	**0.131**
W31	0.448	79.2	**0.283**

A key factor that will be involved in actual supernatant processing will be the ratio of rinse water generated from sludge-washing to the supernatant currently stored in the tanks. If the rinse water dominates the overall mass fraction of supernatant, chemical stabilization of the supernatants will likely be required. Additional characterization data for the supernatants currently present in the tanks would enable a more accurate prediction of potential pass/failure.

Availability of samples for further testing. We expect to have enough sample collected/stored from the MVST tanks to complete this work. In hindsight, liquid supernate samples should have been collected for analysis since very few recent data exist regarding its composition.

Future Work/Test Plan

Based on the most recently collected data and discussions with participants at this review meeting, the following tasks are to be completed during FY00:

Preliminary Supernatant/Rinse TCLPs. We have stored enough rinse from prior sludge-washing to perform at least one TCLP on each tank rinse. We will apply the baseline 'Optimum' process to five worst-failing rinses, which will involve adding chemical stabilization agents after the normal evaporation step. If enough rinse water is left from these intial tests, we will apply the 'Modified Optimum' process to W26 and W27 tank rinses. Due to potential crystallization during supernate evaporation, which could prevent contact of the stabilizing agents with the metal bad actors, FWENC became concerned that the normal 'Optimum' process should be modified. This modification, which we refer to as 'Modified Optimum' has not been received in writing by EM-50 representatives or the project PI but was stated at this review meeting. These data should be available by mid-March, 2001. Based on the outcome, additional testing will be required for verification purposes.

Retesting of W23 Surrogate Rinse. Because substantial data scatter was noted from the triplicate runs of the 'Optimum' process, we will re-run these tests to better understand how the chemical stabilization affects the TCLP response. These data should be available in late February, 2001.

Long Term Testing. Ongoing tests as previously outlined will continue throughout the remainder of FY00. In particular, radiation durability tests of the stabilized W23 Surrogate Sludge and long term environmental performance will be measured. Details may be found in the above sections.

Late Year MVST Work. Based upon the results obtained from preliminary TCLP screens of stabilized supernate rinses, further tests with actual sludge samples are expected. FWENC may have to alter their process for treatment of tank sludges such that retesting of sludge samples will have to be performed late in FY01. These tests cannot be outlined until preliminary screens with the rinses are completed, since the rinse water is likely affecting the sludge TCLP results. Process input from FWENC will likely be required. We may able to determine speciation effects associated with Thio-Red by adding soluble mercury species to sludge samples—such experiments would not be conducted until the preliminary results are finished.

Conclusions

The FWENC 'Optimum' process failed to stabilize mercury levels in two of the six MVST sludge samples. Based on surrogate results, it is unlikely that the 'Alternative' process will enhance stabilization of mercury in those sludges. All other 'bad actor' metals are stabilized effectively.

In addition to routine quantification data, visual observations of work completed with both surrogates and actual sludges should be reported for all future work. Some of the observations may be important for larger-scale process decisions.

Future testing of supernate/rinses from the MVST has been planned and should be completed by late March. Re-testing of some of the surrogate/rinse data will be completed to eliminate uncertainty caused by data scatter. Long term stabilization testing of treated surrogate sludge will continue during FY01.

Attendees

John Barton, ORNL
Tim Hallman, FWENC
Bill Holtzscheiter, SRTC-TFA
John Kinlaw, FWENC
Christine Langton, SRTC-TFA
Jim Moore, Bechtel Jacobs
Jacquie Noble-Dial, Jr, DOE-ORO
Brian Oakley, Duratek
Gary Riner, DOE-ORO
Bryan Roy, FWENC
Roger Spence, ORNL
Bill Zulliger, Bechtel Jacobs