WASTE FORM QUALIFICATION PROGRAM
FOR CEMENT SOLIDIFICATION
OF SLUDGE WASH LIQUID

WEST VALLEY
DEMONSTRATION PROJECT

VOL. 1 OF 2

ISSUED 4/16/92

VOLUME I
WASTE FORM QUALIFICATION PROGRAM FOR CEMENT SOLIDIFICATION OF SLUDGE WASH LIQUID

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WVNS-TP-030	FULL SCALE CONFIRMATION OF THE NOMINAL RECIPE OF SLUDGE WASH LIQUIDS	0	COMPLETE
WVNS-TSR-030	TEST SUMMARY REPORT ON FULL-SCALE CONFIRMATION OF NOMINAL RECIPE FOR SLUDGE WASH LIQUID		FORECAST 4/30/92

West Valley Demonstration Project

Doc. Number WVNS-TPL-70-11

Revision Number 1

Revision Date 09-05-91

Engineering Release #2044
ECN #4534

TEST PLAN

FOR THE WASTE FORM QUALIFICATION PROGRAM FOR
CEMENT SOLIDIFICATION OF SLUDGE WASH LIQUID

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RECORD OF REVISION

PROCEDURE

If there are changes to the procedure, the revision number increases by one. These changes are indicated in the left margin of the body by an arrow (>) at the beginning of the paragraph that contains a change.

Example:

> The arrow in the margin indicates a change.

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0	Original Issue	All	03-25-91
1	Per ECN - 4534	2 thru 4	09-05-91

RECORD OF REVISION (CONTINUATION SHEET)

Rev. No.	Description of Changes	Revision on Page(s)	Dated

WVNS-TPL-70-11

TEST PLAN FOR THE WASTE FORM QUALIFICATION PROGRAM FOR CEMENT SOLIDIFICATION OF SLUDGE WASH LIQUID

REV. 1

1.0 PURPOSE

The purpose of this test plan is to describe the Waste Form Qualification Program for Cement Solidification of Sludge Wash Liquid. The plan specifies the testing required to develop and qualify a stable waste form in accordance with the requirements of 10 CFR 61, Code of Federal Regulations, Title 10, "Licensing Requirements for Land Disposal of Radioactive Waste" and the USNRC Branch Technical Position on Waste Form, Revision 1, draft dated December 1990.

2.0 APPLICABILITY

This program applies to the qualification testing required to demonstrate that the waste form developed herein for the Sludge Wash waste stream meets the waste stability criteria of 10CFR61.56. The scope includes the experimental work performed from waste characterization through full-scale testing in the Cement Solidification System (CSS).

3.0 GENERAL REQUIREMENTS

3.1 All procedures for conducting tests and documenting and evaluating test results will be prepared, reviewed, and approved in accordance with the requirements of the WVNS Policy and Procedure Manual, Engineering Procedures EP-11-001, EP-11-003, and SOP 00-2.

3.2 Test requirements will be as specified in Test Requests (TRQ) issued by the IRTS Process Control Engineering organization in accordance with EP-11-003.

3.3 Testing in response to the Test Resquests shall be performed in accordance with the Test Procedures (TP) issued by the Analytical & Process Chemistry Laboratory in accordance with EP-11-003.

3.4 Operation of the Cement Solidification System (CSS) will be by qualified CSS Operations personnel in accordance with SIP 91-1 and existing Standard Operating Procedures (SOP's).

3.5 Lab testing will be performed by qualified Analytical & Process Chemistry Technicians using Analytical Chemistry Methods (ACM's).

3.6 All data collection, reporting, and documentation will be performed in accordance with EP-11-001 and EP-11-003 as applicable.

4.0 SCOPE

4.1 The scope of the qualification program will be as described in documents summarized in the flowchart (Figure 1).

4.2 Nominal Recipe Development (WVNS-TRQ-025)

Development of the "nominal" recipe will include determination of the "nominal" Water-to-Cement Ratio, as well as the "nominal" addition rates for the recipe enhancers: Calcium Nitrate, Antifoam, and Sodium Silicate.

4.3 Waste Form Qualification (WVNS-TRQ-026)

Qualification of the "nominal" recipe will include establishing a curve of compressive strength vs. time, determination of the maximum practical compressive strength, verification of compressive strength after thermal cycling, determination of resistance of leaching of radionuclides, and verification of compressive strength after immersion.

4.4 Full-Scale Verification (WVNS-TRQ-030)

Full-scale verification of the "nominal" recipe will take place after curing of the full-scale drums processed under SIP 91-1. The drums will be core-drilled, and the cores will be evaluated for compressive strength, as well as compressive strength after immersion.

4.5 Development of Process Control Parameters (WVNS-TRQ-028)

Recipe boundaries will be determined for the following parameters, as a minimum: Total Dissolved Solids (TDS) in the waste stream, Water-to-Cement Ratio, variations in the Cement/Calcium Nitrate Blend, amount of Antifoam recipe enhancer, and the amount of Sodium Silicate recipe enhancer.

The effects of variations in the waste stream will be evaluated for the following parameters: Aluminum content, Sodium content, Organics, Sulfates, pH, Nitites, and Phosphates.

> Plackett-Burman Screening Tests (WVNS-TP-028A)

> 28 cubes will be produced from 28 solutions representing variations in the liquid waste chemical compositions and recipe enhancers. These cubes will be used to screen the degree of interaction between 13 individual components.

> The effects of variations will be evaluated for: bleedwater, gel time, and penetration resistance.

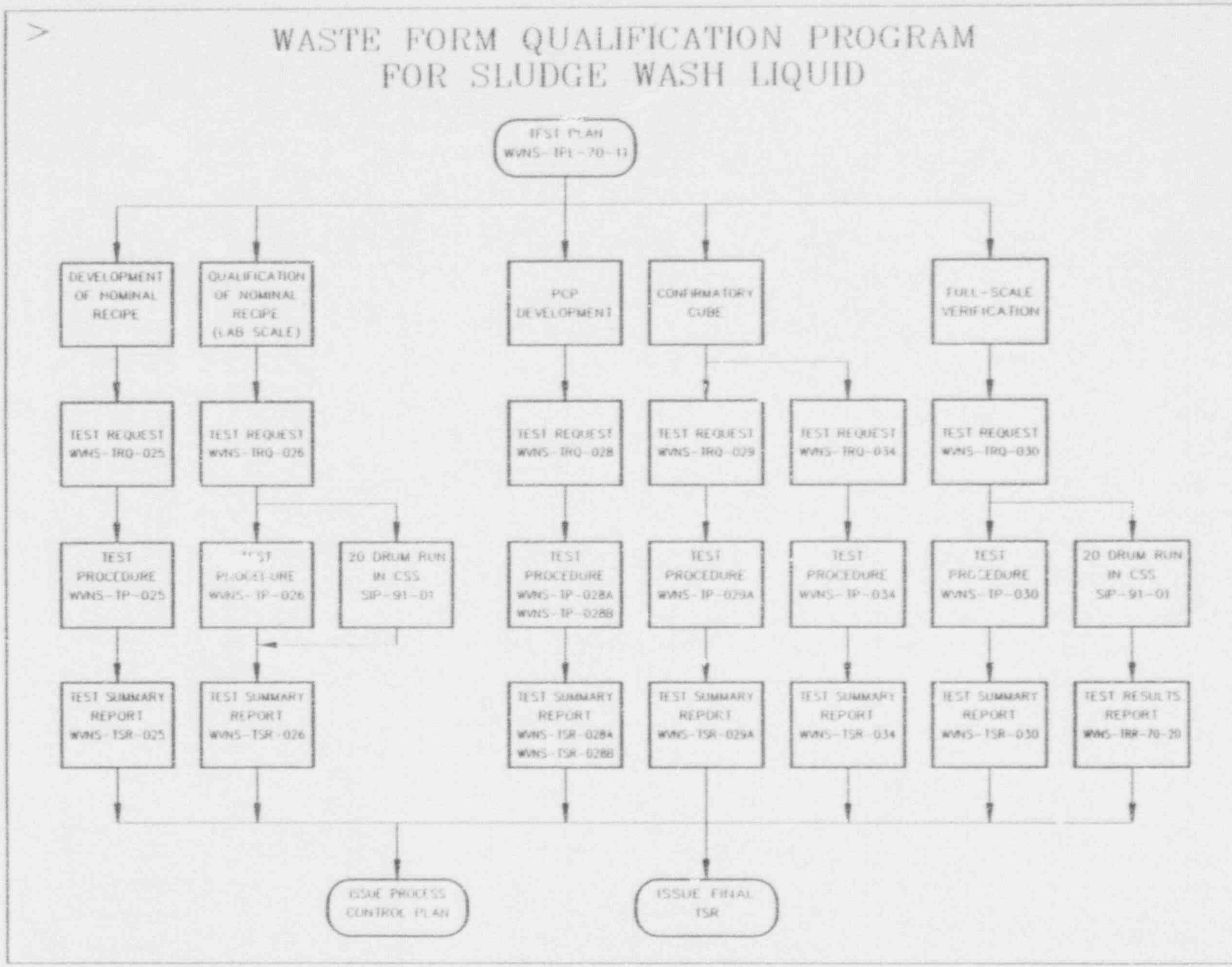
> Box-Behnhen Tests (WVNS-TP-0289B)

> Based on the results of WVNS-TP-028A above, additional tests of the key variables (those with significant interactions) will be conducted to precisely define the recipe limits for each key variable.

4.6 Confirmatory Testing (WVNS-TRQ-029)

For this test, a quantity of actual High Level Waste Tank Sludge will be decontaminated in the laboratory, and the resulting liquid will be solidified using the "nominal" recipe. The compressive strength of the solidified sample will be determined.

Figure 1


WASTE FORM QUALIFICATION PROGRAM
FOR SLUDGE WASH LIQUID
TEST PLAN WVNS-TPL-70-11
DEVELOPMENT OF NOMINAL RECIPE
QUALIFICATION OF NOMINAL RECIPE (LAB SCALE)
PCP DEVELOPMENT
CONFIRMATORY CUBE
FULL-SCALE VERIFICATION
TEST REQUEST WVNS-TRQ-025
TEST REQUEST WVNS-TRQ-026
TEST REQUEST WVNS-TRQ-028
TEST REQUEST WVNS-TRQ-029
TEST REQUEST WVNS-TRQ-034
TEST REQUEST WVNS-TRQ-030
TEST PROCEDURE WVNS-TP-025
TEST PROCEDURE WVNS-TP-026
20 DRUM RUN IN CSS SIP-91-01
TEST PROCEDURE WVNS-TP-028A WVNS-TP-028B
TEST PROCEDURE WVNS-TP-029A
TEST PROCEDURE WVNS-TP-034
TEST PROCEDURE WVNS-TP-030
20 DRUM RUN IN CSS SIP-91-01
TEST SUMMARY REPORT WVNS-TSR-025
TEST SUMMARY REPORT WVNS-TSR-026
TEST SUMMARY REPORT WVNS-TSR-028A WVNS-TSR-028B
TEST SUMMARY REPORT WVNS-TSR-029A
TEST SUMMARY REPORT WVNS-TSR-034
TEST SUMMARY REPORT WVNS-TSR-030
TEST RESULTS REPORT WVNS-TRR-70-20
ISSUE PROCESS CONTROL PLAN
ISSUE FINAL TSR

5.0 DESCRIPTION

5.1 Mixing of lab-scale specimens shall be performed under conditions which duplicate the full-scale mixing conditions mixer speed, mix time, etc., to the maximum extent practical, as discussed in the Branch Technical Position, Appendix A.III.A.

5.2 Curing of lab-scale specimens shall be performed under conditions which duplicate the full-scale curing conditions to the maximum extent practical, as discussed in the Branch Technical Position, Appendix A.III.B. The centerline temperature vs. time of a full-scale drum will be established, and this profile will be followed to the maximum extent practical.

5.3 Compressive strength testing of 2" x 2" x 2" cubes will be performed in accordance with the applicable steps of ASTM Standard C-109.

5.4 Compressive strength testing of cylinders (both cast and core-drilled) will be performed in accordance with the applicable steps of ASTM Standard C-39 and the Branch Technical Position, Appendix A.II.B.

5.5 Testing of thermal stability will be performed in accordance with the applicable sections of ASTM Standard B-553 as discussed in the Branch Technical Position, Appendix A.II.C.

5.6 Resistance to leaching of radionuclides will be performed in accordance with section C.2.e of the main body of ANSI/ANS 16.1, as discussed in the Branch Technical Position, Appendix A.II.F. Prior to leach testing, the most aggressive leachant, deionized water or synthetic sea water will be determined by a 24-hour test.

5.7 Development of process control parameters will be performed in accordance with existing ACM's, and as discussed in the Branch Technical Position, Appendix A.VI.A.

5.8 Immersion testing will be performed in accordance with the Test Procedures (TP's) for that work, and as discussed in the Branch Technical Position, Appendix A.II.G. The immersion testing will be performed using the most aggressive leachant (deionized water or synthetic sea water) as determined in section 5.6 above. Immersion testing may take place for up to 180 days, as discussed in the Branch Technical Position.

5.9 Waste test specimens shall have less than 0.5 percent by volume of the waste specimen as free liquid as discussed in the Branch Technical Position, Appendix A.II.H. Any free liquid encountered shall have a pH greater than or equal to 9.

5.10 Sufficient samples shall be tested to provide enough data to establish a mean and a standard deviation, as discussed in the Branch Technical Position, Appendix A.IV

5.11 Irradiation testing of the waste form will NOT be performed, because no ion exchange resins or other organic media are contained in the waste stream, as discussed in the Branch Technical Position, Appendix A.II.D.

5.12 Biodegradation testing of the waste form will NOT be performed, because the waste liquid contains no carbonaceous materials, as discussed in the Branch Technical Position, Appendix A.II.E.

6.0 REFERENCES

6.1 10CFR61: Code of Federal Regulations, Title 10, Part 61, "Licensing Requirements for Land Disposal of Radioactive Waste"

6.2 ASTM C-39: Standard Test Method for Compressive Strength of Cylindrical Concrete Specimens

6.3 ASTM C-109: Standard test Method for Compressive Strength of Hydraulic Cement Mortars Using 2 inch or 50 mm Cube Specimens

6.4 ASTM B-553: Test Method for Thermal Cycling of Electroplated Plastics

6.5 ASTM C-617: Standard Practice for Capping Cylindrical Concrete Specimens

6.6 ANSI/ANS 16.1: Standard Measurement of the Leachability of Solidified Low-Level Radioactive Wastes by a Short-term Procedure

"SUBMIT DATA SHEET(S)"

UNCONTROLLED COPY
DO NOT USE FOR WORK

Applicable Field Changes ________

SIP 91-01

LWTS/CSS INTEGRATED TEST

Rev. 0

Approved [signature] IRTS Operations Manager

Approved J. C. Cunynon Process Control Engineering Manager

Date 4-30-91

Date 4/30/91

Approved [signature] for P.A.S. Radiation and Safety Manager

Approved [signature] Quality Assurance

Date 5-1-91

Date 5/2/91

THIS PROCEDURE EXPIRES 07/31/91. AFTER THIS DATE, DISCARD EXCEPT FOR MASTER FILE AND COMPLETED WORK COPY

System Quality Level C

System Safety Class C

The estimated accumulated dose for the work described in this document is less than 100 mrem.

WEST VALLEY NUCLEAR SERVICES CO., INC.

May, 1991

Prepared by: [signature]
M. N. Baker

BEL0019:8RM

RECORD OF REVISION

PROCEDURE

If there are changes to the procedure, the revision number increases by one. These changes are indicated in the left margin of the body by an arrow (>) at the beginning of the paragraph that contains a change.

Example:

> The arrow in the margin indicates a change.

Procedure No. SIP 91-01, Rev. 0 Date: May 1991

Rev. No.	Description of Changes	No. of Page	Dated
0	Initial Document	All	05/91

RECORD OF REVISION (CONTINUATION SHEET)

Rev. No.	Description of Changes	No. of Page	Dated

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FULL-SCALE VERIFICATION TEST

1.0 SCOPE

The objectives of the full-scale verification test of CSS are:

1.1 Verify that the full-scale waste forms produced from simulated sludge wash solutions in the CSS meet the requirements of waste stability per 10 CRF 61.56 by checking for free liquid, fill level, and penetration resistance per SOP 70-40.

1.2 Verify that the CSS consistently operates within the limits set by WVNS-TRQ-028, "Test Request for Development of the Process Control Parameters for Cement Solidification of Sludge Wash Liquids."

1.3 Verify the ability of the process instrumentation to measure and document process control parameters.

1.4 Verify that test results for specimens obtained by core sampling full-scale products correlate with test results for laboratory scale specimens produced during the Qualification Test Program, WVNS-TRQ-026.

Correlation will be accomplished by performing (1) compressive strength testing on as-cured material (cured a minimum of 28 days) and (2) 90-day immersion tests that include pre- and post-immersion compressive strength tests in accordance with the USNRC Branch Technical Position on Waste Form, (reference 4.3.36) section C.2.h, and appendix A.

1.5 Verify that the full-scale waste forms demonstrate the stability requirements of the USNRC Branch Technical Position on Waste Form, (reference 4.3.36) appendix A, and WVNS-TRQ-030.

1.6 Produce test specimens (40 cubes 2"x 2"x 2" and 50 cylinders 3" Diameter x 6" long)

1.7 This SIP will be conducted in accordance with WVNS-PCP-001, Rev. 4.

2.0 DEFINITIONS AND ABBREVIATIONS

2.1 Definitions

2.1.1 Programmable Logic Controller - Logic Controller that controls the automatic operation of the CSS using program logic rather than hardwired logic.

2.1.2 Data Acquisition System - Computer based system which monitors and records the outputs of selected CSS instrumentation.

2.1.3 Total Dissolved Solids - concentration of dissolved salts usually expressed as parts per million (ppm) or weight percent (w/o or wt. %).

2.2 Abbreviations

A&PC - Analytical and Process Chemistry
WDV - Waste Dispersing Vessel
CSS - Cement Solidification System
DAS - Data Acquisition System
IWP - Industrial Work Permit
LWTS - Liquid Waste Treatment System
PCE - Process Control Engineer

RWP - Radiation Work Permit

R&S - Radiation and Safety

SSS - Start-up Shift Supervisor

TDS - Total Dissolved Solids

3.0 RESPONSIBILITIES

3.1 Integrated Radwaste Treatment System (IRTS) Operations performs the testing required by this procedure and completes the data sheets to document the procedure.

3.2 IRTS Support Engineering provides technical support as necessary.

3.3 Process Control Engineering (PCE) provides technical direction during testing and checkout, compares the test generated data to Test Plan WVNS-TPL-70-011, and issues Test Results Reports.

3.4 QA provides surveillance to assure that the requirements of this procedure are satisfied, and signs to indicate verification of work performed and data collected.

3.5 The Radiation and Safety Department (R&S) monitors radiation and contamination levels.

3.6 Equipment is repaired as necessary according to EP-11-001, or by SOP 002 as applicable.

3.7 Waste Management Operations performs filled drum movements to the drum cell and core-boring per WVNS-TP-030.

3.8 A&PC analyze and verify satisfactory simulant chemical makeup.

4.0 TOOLS, EQUIPMENT, COMPONENTS AND REFERENCES

4.1 Tools And Equipment

Intercom System

Solid Sample(s) Transport Container(s)

Forney Compressive Strength Testing Equipment

Lifting and rigging equipment

Disposable Plastic 2" x 2" x 2" Cube Sample Molds

Plastic 3" dia. X 6" high cylinder sample molds

Controlled-Temperature Chamber

4.2 Components

CSS - All Cement/Waste mixing equipment fully operational

4.3 References

4.3.1 SOP 70-1 Waste Transfer to the Cement Solidification System

4.3.2 SOP 70-3 Automatic Solidification Operation

4.3.3 SOP 70-4 CSS Manual Solidification with the Process Logic Controller Operational

4.3.4 SOP 70-5 Gravimetric Feeder Operation

4.3.5 SOP 70-6 Bulk Cement Transfer to Day Bin

4.3.6 SOP 70-7 Cement Truck Unloading

4.3.7 SOP 70-8 Clean Drum Handling for Cement Solidification System

4.3.8 SOP 70-9 Automatic Drum Processing Operation

4.3.9 SOP 70-10 Full Drum Handling For CSS

4.3.10 SOP 70-11 Cement Solidification System Manual Operation with Process Logic Contioller Non-operational

4.3.11 SOP 70-12 CSS Mixer System Flush Operation

4.3.12 SOP 70-17 Manual Drum Operations for the CSS

4.3.13 SOP 70-18 Alarm Procedure for Cement Solidification System

4.3.14 SOP 70-19 CSS Emergency Procedure - Emergency Shutdown

4.3.15 SOP 70-30 CSS Stack Sampler and Monitor System Operation

* 4.3.16 SOP 70-31 ATI System Alarm Responses

4.3.17 SOP 70-32 Operation of the CSS Silo Air Dryer

4.3.18 SOP 70-33 Data Acquisition System Operation

4.3.19 SOP 70-34 Operation of the 01-14/CSS Process Room 4-Ton Bridge Crane

4.3.20 SOP 70-35 Operation of Maintenance 2-Ton Bridge Crane

4.3.21 SOP 70-36 Drum Cell Crane Operation

4.3.22 SOP 70-37 Smear Robot Operation

4.3.23 SOP 70-39 Draining and Flushing the WDV

4.3.24 SOP 70-40 CSS Drum Sampling Station Operation

4.3.25 SOP 70-41 CSS Preventive Maintenance Program

4.3.26 SOP 70-42 CSS Safe Shutdown During an Emergency Situation

4.3.27 SOP 70-43 Emergency Emptying of CSS Mixers

4.3.28 SOP 70-45 Waste Classification

4.3.29 SOP 70-46 Operation of the Sodium Silicate Delivery System

4.3.30 SOP 002 Guidelines for the Preparation of Facilities Work Instruction Documents

4.3.31 SOP 004 Lock and Tag Procedure

4.3.32 EP 11-001 Test Control

4.3.33 WV-222 Trouble Records

4.3.34 TPL 70-11 Test Plan for the Waste Form Qualification Program for Cement Solidification of Sludge Wash Liquid

4.3.35 WVNS-PCP-001 [illegible]ess Control Plan for Cement Solidification of Decontam[illegible] [illegible]pernatant

4.3.36 DOE ORDER 582[illegible]a), Radioactive Waste Management

4.3.37 US NRC Branch Technical Position on Waste Form, Rev. 1 dated January, 1991

4.3.38 WVNS-TP-026, Test Procedure for Waste Form Qualification of the Nominal Recipe for Cement Solidification of Sludge Wash Liquid

4.3.39 WVNS-TP-030, Test Procedure for Full-Scale Verification of the Nominal Recipe for Cement Solidification of Sludge Wash Liquid

5.0 GENERAL INFORMATION

5.1 Simulant mixed for this testing shall be transferred to the WDV in the CSS for solidification.

5.2 This Waste Stream shall be solidified in the CSS using recipes developed at Analytical and Process Chemistry, and listed in WVNS-PCP-001, Rev. 4. All operations shall be conducted per System 70 SOPs.

5.3 Cube samples and cast cylinders will be obtained from these drums and destructively tested. This testing will be performed in accordance with WVNS-TP-026.

5.4 Core samples obtained from these drums after curing a minimum of 28 days will be destructively tested in accordance with WVNS-TP-030.

5.5 OPERATORS SHOULD PERFORM FREQUENT CHECKS ON SYSTEMS THAT ARE TURNED ON OR SHUT DOWN TO ASSURE THAT THE SYSTEM DOES WHAT IS EXPECTED, I.E., WATER FLOWS, PRESSURE RISES, LEVEL INDICATORS, ETC. IF THE REQUIRED ACTION THAT IS SUPPOSED TO HAPPEN DOES NOT HAPPEN, (1) STOP - DO NOT ATTEMPT TO PERFORM THE NEXT STEP, (2) SECURE SYSTEM IN A SAFE MODE, AND (3) NOTIFY SHIFT SUPERVISOR IMMEDIATELY.

6.0 PROCEDURE

ALL STEPS IN THIS PROCEDURE THAT REQUIRE AN INSPECTION, THE RECORDING OF DATA, OR A SIGN-OFF WILL BE DENOTED BY A [+] IN THE LEFT-HAND MARGIN. THE INSPECTION RESULTS, DATA, OR SIGN-OFF WILL BE RECORDED ON THE APPROPRIATE PROCEDURE DATA SHEET(S).

6.1 Prerequisites

[+] 6.1.1 Notify PCE and QA prior to performing any testing. Obtain an RWP and IWP to perform drum testing.

[+] 6.1.2 Shift Supervisor or Shift Engineer verify SOPs listed in Section 4.3 are current.

[+] 6.1.3 Record Serial Num er and Calibration Data for Scales used in Section 6.2 on attachment A.

6.2 Simulant Preparation

6.2.1 Mix cold test chemicals in accordance with the following simulant recipe:

Chemical	Symbol	Weight	Source
Sodium Nitrate	$NaNO_3$	286.3#	P.O. 49405
Sodium Nitrite	$NaNO_2$	272#	P.O. 49408
Sodium Sulphate	Na_2SO_4	169.9#	P.O. 49871
Potassium Nitrate	KNO_3	17.9	P.O. 49406
Sodium Carbonate	Na_2CO_3	48.4	P.O. 49406
Sodium Hydroxide	NaOH	1.77	P.O. 49409
Sodium Bichromate	Na_2CrO_4	2.48	P.O. 49871
Sodium Chloride	NaCl	1.88	From VIT
Sodium Phosphate	$NaPO_4$	1.53	P.O. 49409
Sodium Molybdate	Na_2MoO_4	0.33	P.O. 49871
Sodium Tetraborate	Na_3BO_3	0.19	P.O. 49871
Citric Acid	-	0.26	P.O. 49920
Oxalic Acid	-	0.26	P.O. 49920
Tartaric Acid	-	0.26	P.O. 49920
Demineralized Water	H_2O	200 gallons	

6.2.2 Mix the chemicals and water in the tank and piping setup erected under separate work order (WO-9100084).

[+] 6.2.3 Obtain a sample of the simulant. Record lab analysis number on attachment A. A&PC verify satisfactory.

6.3 CSS Operation

6.3.1 Load the gravity feed conveyors with a minimum of 25 square drums per SOP 70-8. Repeat as necessary to keep CSS supplied with empty drums.

6.3.2 Input the required data to the Data Acquisition System per SOP 70-33.

6.3.3 Use the mix tank pump to fill the Waste Dispensing Vessel.

6.3.4 Repeat step as required to keep the WDV liquid level above the low level set point (35 gal .

6.3.5 Use SOP 70-3, to operate the CSS automatically.

6.3.6 When the last batch of waste being processed is in the mix cycle, switch the program selector to "A" to automatically stop the program when the batch is complete.

6.3.7 Use SOP 70-12 to flush the mixers.

6.3.8 Use SOP 70-39 to drain and flush the WDV if required.

6.3.9 Hold the completed drums in the Drum Loadout Area, Transporter, or Process Cell as required.

[+] 6.3.10 Select ten (10) drums for sampling. The ten drums shall be specified by Engineering and QA prior to the production run, and shall be spread out to cover the entire production run. Record drum numbers on attachment B.

[+] 6.3.11 For each drum selected, determine through review of production data if cement/waste mixture was produced within tolerances specified in recipe data sheets and record results on Data Sheet No. 2.

6.4 Thermocouple-Equipped Drum

6.4.1 Equip the first drum processed with thermocouples and temperature recorder as follows:

6.4.2 Insert three (3) thermocouples 10", 20", 30" long through the waste along the drum centerline.

6.4.3 Connect wires to a Molytek recorder

a. Program the recorder to print the temperature at 10-minute intervals

b. Plug the recorder into a 115VAC receptacle in the Drum Loadout Area

c. Locate the recorder near the drum

6.4.4 Equip one (1) of the cylinders cast via step 6.5 with a 6" long K thermocouple (Inconel 600) (no recorder). The instrument that this thermocouple will be connected to must be calibrated to accurately display and/or record temperature sensed by thermocouple.

a. This cylinder will be used as a control cylinder during thermal-cycling testing per WVNS-TP-026

6.4.5 Hold the thermocouple-equipped drum in the Drum Loadout Area until the drum centerline temperature returns to ambient.

6.5 Sampling

6.5.1 After the drum to be sampled is completed, enter the Process Cell and obtain 2" x 2" x 2" cube samples:

a. With the drum at Fill S[illegible]ion M-15, RAISE the fill nozzle

b. Move the drip tray IN

c. Place the cube molds on a towel wipe

d. Scoop the cement/waste product from the drum and fill the cube molds

* FILL THE MOLDS AS FULL AS POSSIBLE *

e. Place the molds in a poly bag containing wipes

f. Label the bag with the drum number, date, and time

6.5.2 Obtain 3" diameter x 6" [illegible]ng cylindrical samples as follows:

a. Place the cylinder molds on a towel wipe

b. Scoop the cement/waste product from the drum and fill the cylinder molds

* FILL THE MOLDS AS FULL AS POSSIBLE *

c. Place the molds in a poly bag containing wipes

d. Label the bag with the drum number, date, and time

6.5.3 Repeat for a total of forty (40) cubes from up to ten (10) drums.

* DO NOT OBTAIN MORE THAN TEN (10) CUBES FROM A DRUM *

6.5.4 Repeat for a total of fifty (50) cylinders from up to ten (10) drums.

* DO NOT OBTAIN MORE THAN TEN (10) CYLINDERS FROM A DRUM *

5.5.5 Release the bagged samples for transfer to the controlled-temperature chamber for curing in accordance with WVNS-TP-026.

6.6 Test Completion

6.6.1 Flush the remaining simulant and chemicals f m the mixing tank to the waste dispensing vessel.

6.6.2 When the last batch of simulant has been processed, flush the mixers per SOP 70-12, and shut down the CSS.

[+] 6.6.3 Shift engineer verify all open items, TRs and TEs have been closed out.

[+] 6.6.4 QA representative verify.

7.0 ATTACHMENTS

7.1 Attachment A: Prerequisites and Test Completion - Data Sheet No. 1

7.2 Attachment B: Data Sheet No. 2

7.3 Attachment C: Core Sampling Locations

ATTACHMENT A

PREREQUISITES AND TEST COMPLETION
Data Sheet No. 1

Step Number	Description	Initials/Date
6.1.1	Engineering Notified ________ Time	________
	QA Notified ________ Time	
	RWP Obtained ________	
	IWP Obtained ________	
6.1.2	SOPS Current ________ Y/N	________
6.1.3	Calibration Data	

Item	Serial No.	Last Calibration
________	________	________
________	________	________
________	________	________
________	________	________
________	________	________

6.2.3 Simulant Sample Results:

Sampled by ________ Operator/Date

Sample Results

Lab Analysis No. ________

Results Acceptable ________ A&PC/Date

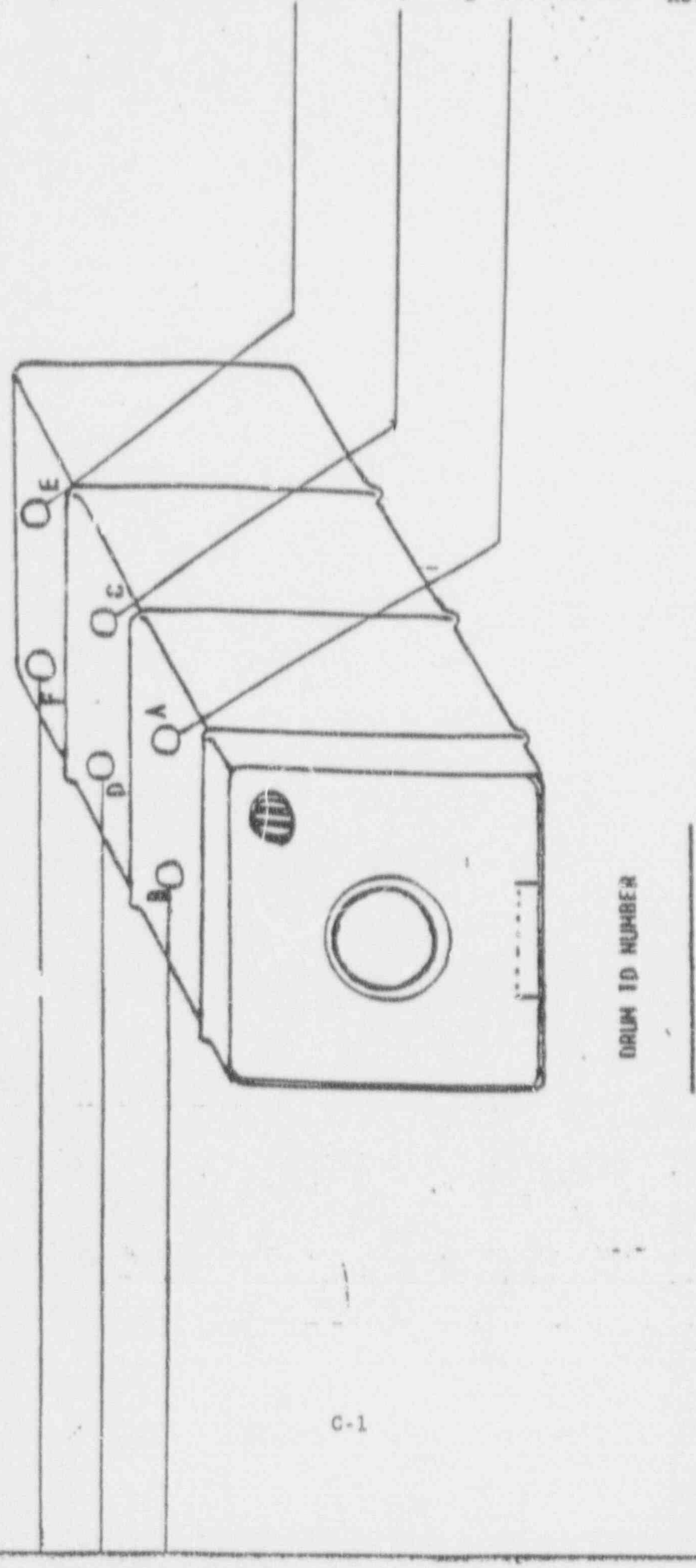
6.6.2 Shift Engineer verify all test exceptions, trouble records, open items are closed out ________ Engineer/Date

6.6.3 QA Verification ________ QA Representative/Date

ATTACHMENT B

Data Sheet No. 2

6.3.10	Drum Number						
	Waste Type						
6.3.11	Drum Weight From M-15 (lbs)						
	Drum Weight From Mixer Load Cell (lbs)						
	Waste Within Tolerance (Yes/No)						


E
C
F
A
D
B
DRUM ID NUMBER

West Valley Demonstration Project

Doc. Number WVNS-TRQ-025

Revision Number 0

Revision Date 04/30/91

Engineering Release #2074

TEST REQUEST

DEVELOPMENT OF THE NOMINAL RECIPE FOR CEMENT SOLIDIFICATION OF SLUDGE WASH LIQUIDS

PREPARED BY [signature] M. N. Baker
Cognizant Engineer

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Process Control Engineering

West Valley Nuclear Services Co., Inc.

P.O. Box 191

West Valley, NY 14171-0191

BEL0046:3RM

WV-1816, Rev. 1

RECORD OF REVISION

PROCEDURE

If there are changes to the procedure, the revision number increases by one. These changes are indicated in the left margin of the body by an arrow (>) at the beginning of the paragraph that contains a change.

Example:

> The arrow in the margin indicates a change.

Rev. No.	Description of Changes	Revision On Page(s)	Dated
0	Original Issue	All	04/30/91

RECORD OF REVISION (CONTINUATION SHEET)

Rev. No.	Description of Changes	Revision on Page(s)	Dated

DEVELOPMENT OF THE NOMINAL RECIPE FOR CEMENT SOLIDIFICATION OF SLUDGE WASH LIQUIDS

1.0 INTRODUCTION

This work is required to develop a stable waste form for cement solidification of Sludge Wash Liquids which meets the characteristics required by 10 CFR 61, Code of Regulations, Title 10, "Licensing Requirements for Land Disposal of Radioactive Waste," and the USNRC Branch Technical Position on Waste Form, Revision 1, dated January 1991.

1.1 All work will be performed in accordance with WVNS-TPL-70-011, the Test Plan for the Waste Form Qualification Program for Cement Solidification of Sludge Wash Liquid (reference 7.3) and related test procedures.

1.2 All work will be performed with a "nominal" simulant representing the actual waste liquid. The composition of the "nominal" simulant was identified by Analytical and Process Chemistry based on Sludge Wash Experimentation (reference 7.1) and Mass Balance Modeling Calculation (reference 7.2). The composition of the "nominal" waste simulant is shown in table 1.

2.0 OBJECTIVE

2.1 Using the simulant liquid, and the existing recipe for supernatant solidification, develop the "nominal" recipe as follows:

a. Characterize the solids in the waste liquids: sulfates, nitrates/nitrites, aluminum, organics, etc.

b. Determine the "nominal" percent solids (by weight) in the waste liquid.

c. Determine the "nominal" range of Calcium Nitrate recipe enhancer to be blended with Portland Type I cement.

d. Determine the "nominal" water-to-cement ratio. Note that this ratio is to be calculated as follows:

$$W/C = \frac{(\text{weight of waste}) \times (1 - \text{solids fraction})}{(1 - \text{Calcium Nitrate fraction}) \times (\text{weight of cement})}$$

e. Determine the "nominal" amount of Antifoam (GE AF9020) recipe enhancer to be added to each batch.

f. Determine the "nominal" amount of Sodium Silicate recipe enhancer.

2.2 At a minimum, slurry density, gel time, free liquid, penetration resistance and compressive strength shall be determine for each specimen.

2.3 The compressive strength of the encapsulated waste shall achieve the maximum practical compressive strength, as required by the Branch Technical Position, appendix A.II.3. A mean compressive strength in excess of 500 psi is required. Lab-scale specimens will be 2" x 2" x 2" cubes in accordance with the applicable steps of ASTM Standard C-109.

2.4 Mixing of the lab-scale specimens shall be performed under conditions approximating the full-scale equipment. Results of lab-scale tests shall be correlated to full-scale test results as described in the Branch Technical Position, appendix A.II.1. Correlation may be limited to compressive strength test results and immersion tests, as discussed in WVNS-TRQ-026.

2.5 Lab-scale specimens shall be cured at 88°C ±2°C, for 61±8 hours, the same conditions as full-scale products, as described in the Branch Technical Position, appendix A.III.B.

2.6 Test specimens shall be kept in sealed containers during curing and storage, to prevent loss of water that might affect the performance of the waste form specimens during subsequent testing, as discussed in the Branch Technical Position, appendix A.III.C.

3.0 SAFETY

3.1 Industrial hygiene practices will be as described in the WVNS Hygiene & Safety Manual, WVDP-011.

3.2 Radiological work will be performed in accordance with the WVDP Radiological Controls Manuals, WVDP-010.

3.3 Work in the Analytical & Process Chemistry lab will be performed in accordance with existing A&PC methods (ACM's).

4.0 EQUIPMENT CONFIGURATION

4.1 All lab equipment will be set up in accordance with WVNS-TP-025, and as directed by the cognizant A&PC scientist or qualified A&PC technician.

5.0 SAMPLING FREQUENCY

5.1 A minimum of ten (10) cube specimens will be produced using the "nominal" recipe as specified by the cognizant A&PC scientist.

6.0 PERSONNEL QUALIFICATION

6.1 Testing will be performed by qualified Analytical & Process Chemistry technicians in accordance with WVNS-TP-025 and using Analytical Chemistry Methods (ACM's) under the cognizance of an A&PC Scientist.

a. Radiochemistry "B" Technicians qualified to WVNS-QS-014.

b. Radiochemistry "A" Technicians qualified to WVNS-QS-016.

6.2 Surveillance activities will be performed by qualified Quality Assurance personnel.

7.0 REFERENCES

7.1 "White Paper on Extraction of Plutonium from .lkaline High Level Liquid Waste," L. A. Bray, F. T. Hara, and T. F. Kazmierczak, Draft C, dated December 21, 1990.

7.2 "Preliminary Flowsheet: Sludge Wash with Existing 8D-2 Heel," letter EK:91:0047, dated March 7, 1991.

7.3 WVNS-TPL-011, Test Plan for the Waste Form Qualification Program for Cement Solidification of Sludge Wash Liquids, M. N. Baker, dated March 25, 1991.

8.0 REPORTING

8.1 The test procedure (WVNS-TP-025) for conducting tests in accordance with this test request shall be issued by the A&PC laboratory.

8.2 A Test Summary Report (TSR) will be issued by the Cognizant Engineer or Cognizant A&PC scientist documenting the results of testing in accordance with Engineering Procedure EP-11-003.

TABLE 1: Salt Concentrations for the "Nominal" Recipe Based on 128.5" Heel

Constituent	Formula	Weight
Sodium Nitrate	$NaNO_3$	35.62
Sodium Nitrite	$NaNO_2$	33.84
Sodium Sulfate	Na_2SO_4	21.13
Sodium Bicarbonate	$NaHCO_3$	*
Potassium Nitrate	KNO_3	2.23
Sodium Carbonate	Na_2CO_3	6.02
Sodium Hydroxide	NaOH	0.22
Sodium Chromate	Na_2CrO_4	0.308
Sodium Chloride	NaCl	0.234
Sodium Phosphate	Na_3PO_4	0.190
Sodium Molybdate	$Na_2MoO_4 \cdot 2H_2O$	0.040
Sodium Borate	$Na_2B_4O_7$	0.024
Citric Acid	$C_6H_8O_7$	0.032
Oxalic Acid	$C_2H_2O_4$	0.032
Tartaric Acid	$C_4H_6O_6$	0.032
Water	H_2O	203.03
	Total Weight	302.982
Weight of Solids		99.952
Weight Percent Solids		33%

* Note: Sodium Bicarbonate does not appear as $NaHNO_3$ at elevated pH s

West Valley Demonstration Project

Doc. Number WVNS-TP-025

Revision Number 0

Revision Date 05/24/91

Engineering Release #2098

TEST PROCEDURE

PROCEDURE FOR DEVELOPMENT OF THE NOMINAL RECIPE FOR CEMENT SOLIDIFICATION OF SLUDGE WASH LIQUIDS

PREPARED BY M. N. Baker
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RECORD OF REVISION (CONTINUATION SHEET)

Rev. No.	Description of Changes	Revision on Page(s)	Dated

PROCEDURE FOR DEVELOPMENT OF THE NOMINAL RECIPE FOR CEMENT SOLIDIFICATION OF SLUDGE WASH LIQUIDS

Rev. 0

1.0 SCOPE

1.1 This work is required to develop a stable waste form for cement solidification of Sludge Wash liquids which exhibits the characteristics required by 10 CFR 61, Code of Federal Regulations, Title 10, "Licensing Requirements for Land Disposal of Radioactive Waste," and the USNRC Branch Technical Position on Waste Form, revision 1, dated January, 1991.

1.2 The recipe for cement solidification of supernatant (DOE/NE/44139-49) will be used as a starting point for this test procedure.

1.3 Work will be performed with a simulant representing the actual waste liquid to develop the "nominal" recipe for solidification of sludge wash liquids.

1.4 A prerequisite for all work will be the decision by the IRTS Restart Task Force as to the actual level of supernatant liquid in High-Level Waste Tank 8D-2: 129-inches.

1.5 A prerequisite for all work will be the determination by the IRTS Restart Task Force of the expected amount of Sulfate in the Sludge Wash Liquid. The composition of the "nominal" recipe, based on letter No. EK:91:0047, is given in table 1.

1.6 Work will be performed using cubes 2" x 2" x 2" cast from a simulant/cement mixture produced in the Analytical Chemistry Lab.

1.7 The "nominal" percent solids (by weight) in the waste liquid will be determined.

1.8 The "nominal" range of Calcium Nitrate recipe enhancer to be blended with Portland Type I cement will be determined.

1.9 The "nominal" water-to-cement ratio will be calculated as follows:

$$W/C = \frac{(\text{Weight of waste}) \times (1 - \text{solids fraction})}{(1 - \text{Calcium Nitrate fraction}) \times (\text{Weight of cement blend})}$$

1.10 Determine the "nominal" amount of Antifoam recipe enhancer to be added to the liquid mixture.

1.11 Determine the "nominal" amount of Sodium Silicate recipe enhancer to be added to the waste/cement mixture.

1.12 The maximum practical compressive strength of the waste form will be determined.

1.13 The effects of variable recipe parameters on the "gel time" and free liquid of the waste mixture will be evaluated.

1.14 The "nominal" recipe developed herein will be scaled up and qualified in accordance with WVNS-TRQ-026. It will also serve as the "nominal" recipe for Process Control Plan parametric window tests being performed under WVNS-TRQ-028.

2.0 DEFINITIONS AND ABBREVIATIONS

2.1 Definitions

Cement - Dry Portland Type I cement in accordance with ASTM Standard C-150-85.

Cement Blend - A homogenous mixture of Portland Type I cement with a percentage of technical grade flake or granular form calcium nitrate with NO ammonium nitrate.

Cast - A specimen mixed in a poly bottle and then poured into a mold.

Cube - A 2" x 2" x 2" cast specimen.

2.2 Abbreviations

ACM - Analytical Chemistry Method
A&PC - Analytical & Process Chemistry
ACP - Analytical Chemistry Procedure
CSS - Cement Solidification System
IRTS - Integrated Radwaste Treatment System
IWP - Industrial Work Permit
PCE - Process Control Engineering
QA - Quality Assurance
R/S - Radiation & Safety
TDS - Total Dissolved Solids

3.0 RESPONSIBILITIES

3.1 Analytical & Process Chemistry performs all work in this Test Procedure.

3.2 Process Control Engineering (PCE) provides technical direction, and compares the test data to the Test Request.

3.3 Quality Assurance provides surveillance to ensure that the requirements of this test procedure are satisfied, and verifies that portions of the test (where independent verification is required) were performed.

3.4 Radiation & Safety monitors radiation and contamination levels

4.0 TOOLS, EQUIPMENT, COMPONENTS, AND REFERENCES

4.1 Tools and Equipment

- "LIGHTNIN" Model TS-1515 lab mixer with high shear impeller
- 2" x 2" x 2" plastic cube molds
- 500 mL poly bottles
- 250 mL poly bottles
- 20 mL scintillation vial
- magnetic stir plate and stirring bar
- timer
- top-loading analytical balance
- Forney Model FT-40-DR compressive strength testing machine with hydraulic power unit and capping set

4.2 Reagents

- Portland Type I cement per ASTM C-150-85
- General Electric AF9020 antifoam emulsion
- Sodium Silicate solution: Water-based solution with 28.5 to 29.5 percent SiO_2
- Powdered calcium nitrate

4.3 Components

- Despatch Series 16000 Environmental Chamber fully operational

4.4 References

4.4.1 EP-11-001, Test Control

4.4.2 EP-11-003, Development Test Control

4.4.3 WVNS-TPL-70-011, Test Plan for Waste Form for Cement Solidification of Sludge Wash Liquids

4.4.4 WVNS-TRQ-025, Test Request for Development of the Nominal Recipe for Cement Solidification of Sludge Wash Liquids

4.4.5 ACM-CEMPREP-4801, Preparation of Cement Samples in the Radiochemistry Lab written by C. W. McVay, et. al.

4.4.6 ACP 7.2, Safety Practices for the Analytical & Process Chemistry Department

4.4.7 WVDP-010, WVNS Radiological Controls Manual

4.4.8 WVDP-011, WVNS Industrial Hygiene & Safety Manual

4.4.9 USNRC Branch Technical Position on Waste Form, revision 1, draft dated December 1990

4.4.10 ASTM Standard C-109, Standard Test Method for Compressive Strength of Hydraulic Cement Mortars (Using 2-inch or 50-mm cube specimens)

4.4.11 ASTM Standard C-617, Practice for Capping Cylindrical Concrete Specimens

4.4.12 ASTM Standard C-470, Specification for Molds for Forming Concrete Test Cylinders Vertically

4.4.13 ASTM Standard C-150, Specification for Portland Type I Cement

5.0 GENERAL INFORMATION

5.1 Performance of the "nominal" waste form developed under this procedure will be qualified under Test Request WVNS-TRQ-026, and Test Procedure WVNS-TP-026.

5.2 Quality Assurance should be notified prior to commencement of activities, in order to perform surveillance(s).

5.3 OPERATORS SHOULD PERFORM FREQUENT CHECKS ON SYSTEMS THAT ARE TURNED ON OR SHUT DOWN TO ASSURE THAT THE SYSTEM DOES WHAT IS EXPECTED, I.E., WATER FLOWS, PRESSURE RISES, ETC. IF THE REQUIRED ACTION THAT IS SUPPOSED TO HAPPEN DOES NOT HAPPEN, (1) STOP - DO NOT PERFORM THE NEXT STEP, (2) SECURE THE SYSTEM IN A SAFE MODE, AND (3) NOTIFY THE COGNIZANT A&PC SCIENTIST OR COGNIZANT ENGINEER IMMEDIATELY.

6.0 EMERGENCY RESPONSE

6.1 For emergencies in the A&PC Lab, responses will be as directed by ACP 7.2 and WVDP-011.

6.2 For emergencies elsewhere in the plant, responses will be as directed by WVDP-010 and WVDP-011.

7.0 DETERMINATION OF THE "NOMINAL" PERCENT SOLIDS IN THE WASTE

This determination will be made by the IRTS Startup Task Force prior to beginning this work.

8.0 DETERMINATION OF THE "NOMINAL" RANGE OF CALCIUM NITRATE RECIPE ENHANCER TO BE BLENDED WITH PORTLAND TYPE I CEMENT

8.1 Starting with the original recipe for encapsulation of Decontaminated Supernatant, test the performance of the waste form at varying percentages of Calcium Nitrate in the cement blend.

8.1.1 Prepare a cube using the "nominal" blend ratio of 5.7 percent Calcium Nitrate in accordance with ACM-CEMPREP-4801.

8.1.2 Cure the cube at 88 $\pm$ 5 degrees celsius for 48 hours.

8.1.3 After curing, remove the cube mold.

8.1.4 Sand two (2) opposite cube faces until flat

8.1.5 Place the cube in the hydraulic press, and measure the pressure at the cube yield point. Record the pressure, and perform the compressive strength calculation per ASTM Standard C-109. Record on form WV-2301.

8.2 Increase the Calcium Nitrate percentage to 6 percent, 7 percent, 8 percent, 9 percent, etc., up to 12 percent Calcium Nitrate in the cement blend.

8.2.1 Prepare cubes at each new cement blend ratio in accordance with ACM-CEMPREP-4801.

8.2.2 Cure the cubes, remove the molds, cap and perform compressive strength testing in accordance with section 8.1.2 through 8.1.5 above.

8.2.3 Record the gel time, penetration resistance, and slurry density on form WV-2301.

8.2.4 Record the presence or absence of bleed water on form WV-2301. If present, determine the pH.

8.3 Decrease the percentage of Calcium Nitrate in the cement to 4 percent.

8.3.1 Prepare the cubes at this cement blend ratio in accordance with ACM-CEMPREP-4801.

8.3.2 Cure the cubes, remove the molds, sand two opposite cube faces until flat and perform compressive strength testing in accordance with sections 8.1.2 through 8.1.5 above.

8.3.3 Record the gel time, penetration resistance, and slurry density on form WV-2301.

8.3.4 Record the presence or absence of bleed water on form WV-2301. If present, determine the pH.

9.0 CALCULATION OF THE NOMINAL WATER-TO-CEMENT RATIO

9.1 After the Calcium Nitrate fraction of the cement blend is determined (section 8.0 above), calculate the nominal water-to-cement ratio as follows:

$$W/C = \frac{(\text{weight of waste}) \times (1 - \text{solids fraction})}{(1 - \text{Calcium Nitrate fraction}) \times (\text{weight of cement blend})}$$

10.0 DETERMINATION OF THE NOMINAL AMOUNT OF ANTIFOAM

10.1 After the nominal Calcium Nitrate fraction in the cement blend and nominal water-to-cement ratio have been determined, the nominal amount of antifoam in the recipe is to be verified.

10.2 With all other recipe parameters remaining the same, or as previously determined in section 8.0 and 9.0 above, prepare a cube in accordance with ACM-CEMPREP-4801.

10.3 Cure the cube at 88 ±5 degrees celsius for 48 hours.

10.4 After curing, remove the cube mold.

10.5 Sand two opposite faces of the cube until flat.

10.6 Place the capped cube in the hydraulic press, and measure the pressure at the cube yield point. Record the pressure, and perform the compressive strength calculation in accordance with ASTM Standard C-109. Record on form WV-2301.

11.0 DETERMINATION OF THE NOMINAL WEIGHT OF SODIUM SILICATE RECIPE ENHANCER TO BE ADDED

11.1 After the Calcium Nitrate fraction in the cement, water-to-cement ratio, and amount of antifoam in the nominal recipe have been determined, the nominal amount of Sodium Silicate additive is to be verified.

11.2 With all other recipe parameters remaining the same, or as previously determined in sections 8.0, 9.0, and 10.0, prepare a cube in accordance with ACM-CEMPREP-4801.

11.3 Cure the cube at 88 ±5 degrees celsius for 48 hours.

11.4 After curing, remove the cube mold.

11.5 Sand two opposite faces of the cube until flat.

11.6 Place the capped cube in the hydraulic press, and measure the pressure at the cube yield point. Record the pressure, and perform the compressive strength calculation per ASTM Standard C-109. Record on form WV-2301.

12.0 DETERMINATION OF THE MAXIMUM COMPRESSIVE STRENGTH

12.1 After the Calcium Nitrate fraction in the cement blend, amount of Antifoam additive, amount of Sodium Silicate, water-to-cement ratio for the nominal recipe have been verified, determine the maximum practical compressive strength of the waste form.

12.2 A mean compressive strength in excess of 500 psi after 28 days curing is desired, as discussed in the Branch Technical Position, appendix A.II.B.

12.3 Sufficient samples shall be prepared to determine the mean compressive strength as well as the standard deviation. A minimum of 10 samples shall be evaluated.

12.4 the compressive strength vs. time will be determined as discussed in WVNS-TP-026, section 7.0.

13.0 CURING

13.1 A curing temperature of 88 ±5 degrees celsius as required for Cement Solidification of Decontaminated Supernatant will be used for initial testing.

13.2 When processing full-scale drums under Work Order 9100084, a drum was equipped with thermocouples and a temperature recorder. The drum temperature as a function of time was plotted. The effect of curing at this temperature profile will be evaluated as discussed in the Branch Technical Position, appendix A.III.B.

13.3 For this procedure, the samples will be bagged and cured in an oven or temperature-controlled chamber.

13.4 The chamber will be equipped with a calibrated thermometer and temperature readings will be continuously recorded.

13.5 All samples will be kept in sealed containers and/or poly bags during curing and storage, as discussed in the Branch Technical Position, appendix A.III.C. This is intended to simulate the environment in a sealed drum.

14.0 <u>DETERMINATION OF "GEL TIMES"</u>

14.1 For all samples cast in the A&PC Lab, the cube molds will be filled in accordance with ACM-CEMPREP-4801, with a 20 mL scintillation vial filled for each cube.

14.2 Visually check for gelation of the cement/waste product in the scintillation vial.

a. Check for gelation every 5 minutes, and do not disturb the vial between these time intervals.

b. Gelation is a subjective determination; however, gelled product is indicated when the 20 mL scintillation vial can be tipped slowly to a 90 degree orientation, and the cement product will not deform or flow, and will retain a line perpendicular to the horizon.

c. Bleedwater is **NOT** to be interpreted as a sign of incomplete gelation. Estimate the quantity and determine the pH if not reabsorbed after 24 hours.

TABLE 1

REVISED SALT CONCENTRATIONS FOR THE "NOMINAL" SIMULANT RECIPE BASED ON 128.5" HEEL

CONSTITUENT	FORMULA	WEIGHT
Sodium Nitrate	$NaNO_3$	286 lbs.
Sodium Nitrite	$NaNO_2$	272 lbs.
Sodium Sulfate	Na_2SO_4	170 lbs.
Sodium Bicarbonate	$NaHCO_3$	*
Potassium Nitrate	KNO_3	17.9 lbs.
Sodium Carbonate	Na_2CO_3	48.4 lbs.
Sodium Hydroxide	$NaOH$	**10.4 lbs.
Sodium Dichromate, Dihydrate	$Na_2Cr_2O_7 \cdot 2H_2O$	1590 g
Sodium Chloride	$NaCl$	1010 g
Sodium Phosphate, Dibasic	Na_2HPO_4	950 g
Sodium Molybdate, Dihydrate	$Na_2MoO_4 \cdot 2H_2O$	226 g
Sodium Tetraborate, Decahydrate	$Na_2B_4O_7 \cdot 10H_2O$	122 g
Citric Acid, Anhydrous	$C_6H_8O_7$	165 g
Oxalic Acid, Anhydrous	$C_2H_2O_4$	129 g
Tartaric Acid, Anhydrous	$C_4H_6O_6$	180 g
Water	H_2O	1668.0 lbs.
	TOTAL WEIGHT	2483.1 lbs.
Weight of Solids		815.1 lbs.
Weight Percent Solids		32.83 percent

* Note that Sodium Bicarbonate does NOT appear as $NaHCO_3$ at elevated pH's.

** The Sodium Hydroxide (NaOH) value is an approximation to arrive at a pH of 12.1. This value may vary.

TEST SUMMARY REPORT

Rev. 0

TEST/TEST SERIES Waste Form Qualification for Cement Solidification of Sludge Wash Liquids

DESCRIPTION Development of the Nominal Recipe for Cement Solidification of Sludge Wash Liquids

TEST REQUEST NO. WVNS-TRQ-025 TEST PLAN NO. WVNS-TPL-70-011

TEST COMMENCEMENT DATE 5/1/91 TEST COMPLETION DATE 5/17/91

Engineering Release #2157

1.0 OBSERVATIONS/COMMENTS:

The purpose of this test procedure was to determine the nominal recipe for cement solidification of sludge wash liquids using the existing recipe for supernatant solidification as a first approximation. This test procedure verified that the existing supernatant recipe will be the nominal recipe used in future testing with the exception that the waste liquid will be 29 to 33% solids instead of 37 to 41% used for supernatant.

2.0 REFERENCES:

1) Letter No. EK:91:0047, "Preliminary Flowsheet: Sludge Wash with Existing 8D-2 Heel", dated March 7, 1991.

2) DOE/NE/44139-49, Topical Report on Development of the Recipe for Solidification of Decontaminated Supernatant, McVay, et. al.

3) USNRC Branch Technical Position on Waste Form, Rev. 1, dated January 1991.

4) Letter No. FH:91:0089, "Test Results on Nominal Recipe Qualification", dated June 21, 1991.

3.0 OBJECTIVES MET:

3.1 **Determine the acceptable range of percent solids (by weight) in the waste liquid.**

STATUS: Complete

OBSERVATION: Increasing the percent solids in the waste liquid above the "nominal" range lowers the compressive strength of the waste form.

DATA: Refer to Table 1

3.2 **Determine the acceptable range of calcium nitrate recipe enhancer to be blended with Portland Type I cement.**

STATUS: Complete

OBSERVATION: The waste form produced with no calcium nitrate in the cement blend exhibited lower compressive strength as well as slow gel times. Large amounts of calcium nitrate in the cement blend also resulted in lower compressive strength.

DATA: Refer to Table 2

3.3 **Determine the acceptable range of water-to-cement ratio.**

STATUS: Complete

OBSERVATION: The waste form exhibits lower compressive strength at high water-to-cement ratios.

DATA: Refer to Table 3

3.4 **Determine the acceptable range of antifoam recipe enhancer to be added to the waste.**

STATUS: Complete

OBSERVATION: None

DATA: Refer to Table 4

3.5 **Determine the acceptable range of sodium silicate recipe enhancer to be added to the waste/cement mixture.**

STATUS: Complete

OBSERVATION: The waste form produced with no sodium silicate exhibited a slow gel time, and bleed water.

DATA: Refer to Table 5

3.6 **Determine the maximum practical compressive strength of the waste form.**

STATUS: Complete

OBSERVATION: The average compressive strength exhibited by the waste form at the "nominal" recipe was 1403 psi, with a 2 sigma (90% confidence band) of 316 psi.

DATA: Refer to Table 6

3.7 **Evaluate the effects of the recipe parameters on "gel time" and free liquid in the waste mixture.**

STATUS: Complete

OBSERVATION: See section 3.2 and 3.5 above.

DATA: Refer to Table 7

4.0 CONCLUSIONS:

4.1 The nominal recipe for supernatant processing will be used for sludge wash waste form qualification testing. This recipe is shown in table 7.

4.2 There is a practical upper limit to the water-to-cement ratio, as well as to the percent solids in the waste stream and calcium nitrate cement blend.

These are three variations of the same effect: cement must be hydrated by water, and any parameter which changes the amount of water (solids in the waste liquid) or cement (calcium nitrate in the blend) will affect the hydration reaction.

5.0 ACCEPTABILITY OF RESULTS:

5.1 The results of this test are acceptable. It is felt that a reasonable number of test specimens were prepared and that the results clearly demonstrate where an effect is encountered.

5.2 The results of tests where no effect is seen are sufficiently close in order of magnitude to establish that no concern is justified.

6.0 ACTIONS OUTSTANDING:

6.1 The exact limits for recipe parameters, as well as the possible interaction of all variables will be evaluated during multi-variant testing as described in WVNS-TP-028.

6.2 Characterization of the solids in the waste liquid, discussed in WVNS-TRQ-025, was not performed, but the effect of sulfates, nitrates, nitrites, aluminum, ect., will be evaluated during WVNS-TP-028/028A.

APPROVAL(S) [signature] (Test Requester) ADDITIONAL REVIEWERS: YES NO

[signature] 7/25/91 J. C. Cwynar | [signature] 7/30/91 J. L. Mahoney. | [signature] 7/3/91 QA

TABLE 1

SAMPLE ID.	GEL TIME (mins)	PENETRATION (psi)	BLEED WATER (mls)	COMP STRENGTH (psi)	SLURRY DENSITY (g/ml)
Total Solids Variations					
SWCF4 28.79%	10	>700	<1	2021	1.75
SWCF4 30.14%	10	>700	<1	1817	1.77
SWCF4 32.23%	5	>700	<1	1601	1.76
SWCF4 34.91%	7	>700	<1	1343	1.79
SWCF4 41.46%	58	>700	<1	859	1.81

TABLE 2

SAMPLE ID.	GEL TIME (mins)	PENETRATION (psi)	BLEED WATER (mls)	COMP STRENGTH (psi)	SLURRY DENSITY (g/ml)
Calcium Nitrate Variations					
SWCF4 NR 0%	7	>700	<1	1054	NA
SWCF4 NR 0%	10	>700	<1	1334	1.80
SWCF4 NR 0%	20	>700	<1	822	1.74
SWCF4 NR 3%	5	>700	<1	1535	1.79
SWCF4 NR 3%	5	>700	<1	1359	1.74
SWCF4 NR 4%	5	>700	<1	1331	1.74
SWCF4 NR 5.7%	5	>700	<1	1581	1.71
SWCF4 NR 9%	5	>700	<1	1518	1.[illegible]
SWCF4 NR 11.4%	5	>700	<1	1274	1.67
SWCF4 NR 17.1%	5	>700	<1	481	1.63

TABLE 3

SAMPLE ID.	GEL TIME (mins)	PENETRATION (psi)	BLEED WATER (mls)	COMP STRENGTH (psi)	SLURRY DENSITY (g/ml)
Water to Cement Ratio					
SWCF4 0.50	5	>700	<1	2174	NA
SWCF4 0.55	5	>700	<1	1731	NA
SWCF4 0.61	5	>700	<1	1434	1.77
SWCF4 0.70	5	>700	<1	1089	NA
SWCF4 0.70	7	>700	<1	1216	1.71
SWCF4 0.80	30	>700	<1	565	NA
SWCF4 0.80	20	>700	<1	788	1.62

TABLE 4

SAMPLE ID.	GEL TIME (mins)	PENETRATION (psi)	BLEED WATER (mls)	COMP STRENGTH (psi)	SLURRY DENSITY (g/ml)
Antifoam Variation					
SWCF4 0 ml	5	>700	<1	1777	1.69
SWCF4 0.075 ml	5	>700	<1	1695	1.78
SWCF4 0.15 ml	5	>700	<1	947	1.76
SWCF4 0.30 ml	5	>700	<1	1443	1.76
SWCF4 0.375 ml	5	>700	<1	1591	1.75
SWCF4 0.45 ml	5	>700	<1	1418	1.75
SWCF4 0.60 ml	5	>700	<1	1479	1.72

TABLE 5

SAMPLE ID.	GEL TIME (mins)	PENETRATION (psi)	BLEED WATER (mls)	COMP STRENGTH (psi)	SLURRY DENSITY (g/ml)
Sodium Silicate Variations					
SWCF4 NR 0 g	10	>700	2	1926	1.80
SWCF4 NR 2.75 g	5	>700	<1	1400	NA
SWCF4 NR 5.09 g	0	>700	<1	1367	1/66
SWCF4 NR 8.25 g	5	>700	<1	1500	1/76
SWCF4 NR 10.04 g	5	>700	<1	1489	1.74
SWCF4 NR 13.75 g	5	>700	<1	1321	1.77
SWCF4 NR 15.38 g	7	>700	<1	1308	NA
SWCF4 NR 16.88 g	20	>700	<1	1281	1.71

TABLE 6

SAMPLE ID.	GEL TIME (mins)	PENETRATION (psi)	BLEED WATER (mls)	COMP STRENGTH (psi)	SLURRY DENSITY (g/ml)
Nominal Recipe					
SWCF4 NR	5	>700	<1	1339	1.73
SWCF4 NR	5	>700	<1	1435	1.71
SWCF4 NR	5	>700	<1	1203	1.74
SWCF4 NR	5	>700	<1	1253	1.75
SWCF4 NR	5	>700	<1	1438	1.70
SWCF4 NR	5	>700	<1	1263	1.75
SWCF4 NR	5	>700	<1	1694	NA
SWCF4 NR	5	>700	<1	1296	NA
SWCF4 NR	5	>700	<1	1303	NA
SWCF4 NR	5	>700	<1	1722	1.75
SWCF4 NR	5	>700	<1	1432	1.77
SWCF4 NR	5	>700	<1	1401	1.76
SWCF4 NR	5	>700	<1	1464	1.77

TABLE 7

PARAMETER	"NOMINAL" RECIPE FOR SUPERNATANT PROCESSING	SATISFACTORY RANGE FROM THIS TEST PROCEDURE
% Solids in Waste	37 to 41%	28.79 to 34.91%
Calcium Nitrate	4.7 to 7.4%	3.0 to 11.4%
W/C Ratio	0.54 to 0.70	0.50 to 0.70
Antifoam	0.30 mL	0 mL to 0.60 mL
Sodium Silicate	10.5 to 11.5 grams	2.75 to 15.3 grams
Compressive Strength	>500 PSI	1403 PSI Average
Gel Time	0 to 90 minutes	5 to 10 minutes

West Valley Demonstration Project

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Engineering Release #2077

TEST REQUEST

WASTE FORM QUALIFICATION WORK FOR THE NOMINAL RECIPE FOR CEMENT SOLIDIFICATION OF SLUDGE WASH LIQUIDS

PREPARED BY _____ M. N. Baker
Cognizant Engineer

APPROVED BY _____ D. C. Meess
Cognizant System Design Manager

APPROVED BY _____ 4/19/91 D. L. Shugars
Quality Assurance Manager

APPROVED BY _____ for D. J. Harward
Radiation and Safety Manager

APPROVED BY _____ 4/19/91 J. C. Cwynar
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BEL0047:3RM

WV-1816, Rev. 1

RECORD OF REVISION

PROCEDURE

If there are changes to the procedure, the revision number increases by one. These changes are indicated in the left margin of the body by an arrow (>) at the beginning of the paragraph that contains a change.

Example:

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RECORD OF REVISION (CONTINUATION SHEET)

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WASTE FORM QUALIFICATION WORK FOR THE NOMINAL RECIPE FOR CEMENT SOLIDIFICATION OF SLUDGE WASH LIQUIDS

1.0 INTRODUCTION

1.1 This work is required to demonstrate the stability of the "nominal" waste form recipe developed under Test Request WVNS-TRQ-025. Characteristics which will be tested are required by the 10 CFR 61, Code of Federal Regulations, Title 10, "Licensing Requirements for Land Disposal of Radioactive Waste," and the USNRC Branch Technical Position on Waste Form, revision 1, dated January, 1991.

1.2 This work is performed as a part of WVNS-TPL-70-011.

1.3 Work will be performed with a simulant representing the actual waste liquid. The simulant is shown in Table 1 and will be verified under WVNS-TRQ-025.

1.4 Work will be performed using both 2" x 2" x 2" cubes and 3" diameter x 6" long cylinders cast from full-scale drums processed in the Cement Solidification System (CSS) under SIP 91-1. The purpose of this is to establish a correlation between the full-scale cylinders, full-scale cubes, and lab-scale cubes. Leach testing specimens will be 1" diameter x 3" high cylinders prepared in the A&PC laboratory using the lab-scale mixer. Leach specimens will be "spiked" with appropriate radionuclides.

1.5 Test Procedure WVNS-TP-026, providing instructions for testing in accordance with this Test Request shall be issued by Analytical and Process Chemistry per EP-11-003.

1.6 Test Summary Report, WVNS-TSR-026, documenting the results of this testing, will be issued by the Cognizant Engineer per EP-11-003.

2.0 OBJECTIVES

2.1 A curve of compressive strength vs. cure time will be established for both cubes and cylinders. The cure time which produces a compressive strength within 75 percent of maximum shall be determined.

2.2 The compressive strength of the waste form as required by the Branch Technical Position, appendix A.II.B will be verified at cure times of 7, 14, 21, 28, 35, and 42 days. A mean compressive strength in excess of 500 psi after 28 days is required.

2.3 Thermal cycling stability of the waste form will be tested in accordance with ASTM Standard B-553, and the Branch Technical Position, appendix A.II.C.

2.4 Resistance to leaching of radionuclides will be performed using a simulant liquid "spiked" with Cesium-137, Strontium 90, and Plutonium 241. Leaching will be performed in accordance with the Branch Technical Position, appendix A.II.F, and ANS/ANSI procedure 16.1. Preliminary testing will be performed to identify the leachant as deionized water or synthetic sea water.

A Leachability Index, calculated in accordance with ANS/ANSI 16.1, greater than 6.0 is required.

2.5 Immersion testing shall be performed in accordance with the Branch Technical Position, appendix A.II.G. After curing for a minimum of 28 days or the cure time as indicated by the compressive strength vs. time testing in paragraph 2.? above, at least three (3) cylinders will be immersed for a period of 90 days. Following immersion, the specimens shall be subjected to compressive strength testing. A mean post-immersion compressive strength not less than 75% of the pre-immersion mean compressive strength (paragraph 2.2 above) is required. If the mean post-immersion compressive strength is less than 75% of the pre-immersion mean compressive strength, the immersion testing interval shall be extended (using different specimens) to 120, 150, and 180 days. This testing is required to establish that the compressive strengths level off and do not continue to decrease with time.

2.6 For one (1) specimen, the leachability of the following "heavy metal" shall be evaluated in accordance with the Toxicity Characteristics Leaching Procedure (TCLP): Chromium.

3.0 SAFETY

3.1 Industrial hygiene practices will be as described in the WVNS Hygiene & Safety Manual, WVDP-011.

3.2 Radiological work will be performed in accordance with the WVDP Radiological Controls Manual, WVDP-010.

3.3 Work in the Analytical & Process Chemistry lab will be performed in accordance with existing A&PC methods (ACM's).

4.0 EQUIPMENT CONFIGURATION

4.1 All lab equipment will be set up in accordance with WVNS-TP-026 and as directed by the cognizant A&PC scientist or qualified A&PC technician.

4.2 Mixing will be performed in a manner which duplicates, to the extent practical, the full-scale mixing equipment, including mixing speed, order of addition, mixing time, energy introduced to the mixture, etc., as discussed in the Branch Technical Position, appendix A.III.A.

4.3 Curing of the samples will be performed in a manner which duplicates, to the extent practical, the curing temperature profile encountered in the full-scale drum, as discussed in the Branch Technical Position, appendix A.III.B. A temperature-controlled chamber will be utilized.

4.4 Calibration of compressive strength testing equipment will be in accordance with the applicable steps of ASTM Method C-39, C-109, and WVNS-QIP-027.

5.0 SAMPLING FREQUENCY

5.1 A total of 40 cubes 2" x 2" x 2" will be required.

5.2 A total of 50 cylinders 3" diameter x 6" high will be required.

5.3 A total of three (3) cylinders 1" diameter x 3" high will be required for Leach testing.

6.0 PERSONNEL QUALIFICATION

6.1 Laboratory testing will be performed by qualified Analytical & Process Chemistry Technicians in accordance with WVNS-TP-026 and Analytical Chemistry Methods (ACM's) under the cognizance of an A&PC Scientist.

a) Radiochemistry "B" Technicians qualified to WVNS-QS-014.

b) Radiochemistry "A" Technicians qualified to WVNS-QS-016.

6.2 Compressive strength testing of cylinders will be performed by Quality Services personnel trained in the requirements of QIP-27.

7.0 DATA REPORTING

7.1 A Test Summary Report (WVNS-TSR-026) documenting the results of testing performed per this test request shall be issued by the Cognizant Test Engineer.

TABLE 1: Salt Concentrations for the "Nominal" Recipe Based on 128.5" Heel

Constituent	Formula	Weight
Sodium Nitrate	$NaNO_3$	35.62
Sodium Nitrite	$NaNO_2$	33.84
Sodium Sulfate	Na_2SO_4	21.13
Sodium Bicarbonate	$NaHCO_3$	*
Potassium Nitrate	KNO_3	2.23
Sodium Carbonate	Na_2CO_3	6.02
Sodium Hydroxide	NaOH	0.22
Sodium Chromate	Na_2CrO_4	0.308
Sodium Chloride	NaCl	0.234
Sodium Phosphate	Na_3PO_4	0.190
Sodium Molybdate	$Na_2MoO_4 \cdot 2H_2O$	0.040
Sodium Borate	$Na_2B_4O_7$	0.024
Citric Acid	$C_6H_8O_7$	0.032
Oxalic Acid	$C_2H_2O_4$	0.032
Tartaric Acid	$C_4H_6O_6$	0.032
Water	H_2O	203.03
	Total Weight	302.982
Weight of Solids		99.952
Weight Percent Solids		33%

* Note: Sodium Bicarbonate does not appear as $NaHNO_3$ at elevated pH s

West Valley Demonstration Project

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TEST PROCEDURE

PROCEDURE FOR QUALIFICATION OF THE NOMINAL RECIPE FOR CEMENT SOLIDIFICATION OF SLUDGE WASH LIQUIDS

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WV-1816, Rev. 1

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RECORD OF REVISION (CONTINUATION SHEET)

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PROCEDURE FOR QUALIFICATION OF THE NOMINAL RECIPE FOR CEMENT SOLIDIFICATION OF SLUDGE WASH LIQUIDS

Rev. 0

1.0 SCOPE

1.1 This work is required to demonstrate the stability of the "nominal" waste form recipe developed under Test Request WVNS-TRQ-025. Characteristics which will be tested are required by 10 CFR 61, Code of Federal Regulations, Title 10, "Licensing Requirements for Land Disposal of Radioactive Waste," and the USNRC Branch Technical Position on Waste Form, revision 1, dated January, 1991. This work is part of WVNS-TPL-70-11, "Test Plan for the Waste Form Qualification Program for Cement Solidification of Sludge Wash Liquid."

1.2 Work will be performed with a simulant representing the actual waste liquid. After all tests have been performed, a small sample of the actual sludge wash product will be solidified using the qualified recipe. This sample will be subjected to compressive strength testing. This work will be performed under WVNS-TRQ-029.

1.3 Work will be performed using both cubes (2"x2"x2") and cylinders (3" diameter x 6" long) cast from full-scale drums processed in the Cement Solidification System (CSS). The purpose of duplicate tests is to establish a correlation between the full-scale cylinders, full-scale cubes, and lab-scale cubes.

1.4 A curve of compressive strength vs. cure time will be established for both cubes and cylinders.

1.5 The maximum practical compressive strength of the waste form will be verified at cure times of 7, 14, 21, 28, 35, and 42 days.

1.6 Thermal cycling stability of the waste form will be tested in accordance with ASTM Standard B-553, section 3.1.

1.7 Resistance to leaching of radionuclides will be performed using a simulant liquid "spiked" with Cesium-137, Strontium-90, and Plutonium-241, in accordance with the Branch Technical Position, appendix A.II.F, and ANSI/ANS Standard 16.1. Preliminary testing will be performed to identify the leachant as deionized water or synthetic seawater.

1.8 After curing for a minimum of 28 days, as indicated by the compressive strength vs. time testing in paragraph 1.4 above, at least three (3) cylinders will be immersed for a period of 90 days. Following immersion, the specimens shall be subjected to compressive strength testing. A mean post-immersion compressive strength not less than 75 percent of the mean compressive strength (paragraph 1.4 above) is required. If the mean post-immersion compressive strength is less than 75 percent of the mean pre-immersion compressive strength, the immersion interval shall be extended (using different specimens) to 120, 150, and 180 days. This testing is required to establish that the compressive strengths level off and do not continue to decrease with time.

1.9 For one (1) specimen, the leachability of the chromium shall be evaluated in accordance with the Toxicity Characteristic Leaching Procedure (TCLP).

2.0 DEFINITIONS AND ABBREVIATIONS

2.1 Definitions

Cement - Dry Portland Type I cement in accordance with ASTM Standard C-150-85

Cement Blend - A homogenous mixture of Portland Type I cement with 5.7 ± 1.7 percent technical grade flake or granular form calcium nitrate with NO ammonium nitrate.

Cast - A cube or cylinder specimen produced in the mixer, then scooped into the mold

Cube - A 2"x2"x2" cast specimen produced either in a lab mixer or the full-scale mixer

Cylinder - A cast specimen 3" diameter x 6" long produced in the full-scale mixer.

Demineralized Water - water having a conductivity less than 5 micromho/cm at 25 degrees Celsius and a total organic carbon content less than 3 parts/million.

Synthetic Seawater - a combination of various inorganic compounds as follows:

Sodium Chloride	23.497 grams
Magnesium Chloride	4.981 grams
Sodium Sulfate	3.917 grams
Calcium Chloride	1.102 grams
Sodium Carbonate	0.192 grams
Potasium Bromide	0.096 grams
Demineralized Water	965.551 milliliters

2.2 Abbreviations

ACM - Analytical Chemistry Method
A&PC - Analytical & Process Chemistry
ACP - Analytical Chemistry Procedure
CSS - Cement Solidification System
DAS - Data Acquisition System
IWP - Industrial Work Permit
IRTS - Integrated Radwaste Treatment System
LWTS - Liquid Waste Treatment System
PCE - Process Control Engineering
QA - Quality Assurance
R&S - Radiation and Safety
SIP - Special Instructions Procedure
SOP - Standard Operating Procedure
TDS - Total Dissolved Solids

3.0 RESPONSIBILITIES

3.1 Integrated Radwaste Treatment System (IRTS) Operations personnel operate the Cement Solidification System (CSS) in accordance with SIP 91-01 and WVNS-PCP-001 to produce the full-scale drums of solidified simulant liquid required for this test procedure.

3.2 IRTS Support Engineering provides technical support as necessary.

3.3 Process Control Engineering (PCE) provides technical direction, and compares the test data to the Test Request requirements.

3.4 Quality Services provides surveillance to ensure that the requirements of this test procedure are satisfied, and verifies that portions of the test (where independent verification is required) were performed.

3.5 Quality Services performs compressive strength testing of cylinders in accordance with QIP-027.

3.6 Analytical & Process Chemistry performs the following: a) chemical analyses required to confirm that the test liquid accurately simulates the sludge wash liquid; b) perform TCLP leach testing for radionuclides; c) perform TCLP leach testing chromium; d) perform thermal cycling test; e) perform immersion test; f) perform compressive strength tests on cubes and cylinders.

3.7 Radiation and Safety (R/S) monitors radiation and contamination levels.

4.0 TOOLS, EQUIPMENT, COMPONENTS, AND REFERENCES

4.1 Tools and Equipment

2" x 2" x 2" poly cube molds

3" diameter x 6" long cylinder molds per ASTM Standard C-470

poly bags

solid sample(s) transport container(s)

5-gallon high density polyethlene pails with lids

20 Liters Demineralized Water

20 Liters Synthetic Seawater

recording thermometer readable to +/- 0.5 degree Celsius

4.2 Components

CSS equipment fully operational

Despatch Series 16000 Environmental Chamber fully operational

Forney Model FT-40-DR Compressive Strength Testing Unit fully operational

4.3 References

4.3.1 CSS (System 70) Standard Operating Procedures

4.3.2 EP-11-001, Test Control

4.3.3 EP-11-003, Development Test Control

4.3.4 WVNS-TPL-70-011, Test Plan for Waste Form for Cement Solidification of Sludge Wash Liquid

4.3.5 WVNS-TRQ-026, Test Request for Waste Form Qualification Work for the Nominal Recipe for Cement Solidification of Sludge Wash Liquid

4.3.6 WVDP-010, WVNS Radiation Controls Manual

4.3.7 WVDP-011, WVNS Industrial Hygiene & Safety Manual

4.3.8 USNRC Branch Technical Position on Waste Form, Revision 1, dated January, 1991

4.3.9 ASTM C-109 Standard Test method for Compressive Strength of Hydraulic Cement Mortars (Using 2-in. or 50-mm Cube Specimens)

4.3.10 ASTM C-39 Standard Test Method for Compressive Strength of Cylindrical Concrete Specimens

3.11 ASTM B-553 Standard Test Method for Thermal Cycling of Electroplated Plastics

4.3.12 ANSI/ANS 16.1 American National Standard Measurement of the Leachability of Solidified Low-Level Radioactive Wastes by a Short-term Procedure

4.3.13 SIP 91-01, LWTS/CSS Integrated Test

4.3.14 QIP-027 Quality Inspection Procedure for Compressive Strength Testing of Cement Cylinders

4.3.15 WVNS-TRQ-029, Test Procedure for Production of Cement Product from Actual Sludge Wash Liquid

4.3.16 WVNS-TRQ-025, Test Request for Development of the Nominal Recipe for Cement Solidification of Sludge Wash Liquids

4.3.17 WVNS-TP-025, Test Procedure for Development of the Nominal Recipe for Cement Solidification of Sludge Wash Liquids

4.3.18 ACP 7.2, Administrative Control Procedure for Laboratory Safety

4.3.19 ACM-4701, Analytical Chemistry Method for Destructive Test of Cement Specimens

4.3.20 ACM-4801, Analytical Chemistry Method for Cement Test Cube Preparation Method

4.3.21 ACM-5901, Analytical Chemistry Method for Toxicity Characteristics Leaching Procedure (TCLP)

4.3.22 ACM-6200, Analytical Chemistry Method for Operation of Despatch Environmental Chamber

4.3.23 ACM-6300, Analytical Chemistry Method for Leach Index of Cement Specimens

4.3.24 ACM-6400, Analytical Chemistry Method for Immersion Testing of Cement Specimens

5.0 GENERAL INFORMATION

5.1 The nominal recipe being qualified by this test procedure will be developed under Test Request WVNS-TRQ-025, and Test Procedure WVNS-TP-025.

5.2 Results of this testing will be compared to the results obtained under WVNS-TRQ-025.

5.3 Quality Assurance should be notified prior to the start of this work.

5.4 OPERATORS SHOULD PERFORM FREQUENT CHECKS ON SYSTEMS THAT ARE TURNED ON OR SHUT DOWN TO ASSURE THAT THE SYSTEM DOES WHAT IS EXPECTED, I.E., WATER FLOWS, PRESSURE RISES, ETC. IF THE REQUIRED ACTION THAT IS SUPPOSED TO HAPPEN DOES NOT HAPPEN, (1) STOP - DO NOT PERFORM THE NEXT STEP, (2) - SECURE THE SYSTEM IN A SAFE MODE, AND (3) - NOTIFY THE COGNIZANT A&PC SCIENTIST OR COGNIZANT ENGINEER IMMEDIATELY.

6.0 EMERGENCY RESPONSE

6.1 For emergencies in the A&PC Lab, responses will be as directed by ACP 7.2 and WVDP-010.

6.2 For emergencies elsewhere in the plant, responses will be as directed by WVDP-010.

7.0 COMPRESSIVE STRENGTH VS. TIME

7.1 After curing 7 days in the controlled-temperature chamber and at room temperature as discussed in section 13.1 below, a total of three (3) cubes will be subjected to compressive strength testing per applicable steps of ASTM Standard C-109 and the applicable steps of ACM-4801.

7.2 After curing 14 days in the controlled-temperature chamber and at room temperature as discussed in section 13.1 below, a total of three (3) cubes will be subjected to compressive strength testing per applicable steps of ASTM Standard C-109 and the applicable steps of ACM-4801.

7.3 After curing 21 days in the controlled-temperature chamber and at room temperature as discussed in section 13.1 below, a total of three (3) cubes will be subjected to compressive strength testing per applicable steps of ASTM Standard C-109 and the applicable steps of ACM-4801.

7.4 After curing 28 days in the controlled-temperature chamber and at room temperature as discussed in section 13.1 below, a total of ten (10) cubes will be subjected to compressive strength testing per applicable steps of ASTM Standard C-109 and the applicable steps of ACM-4801. A compressive strength greater than 500 psi is desired. Refer also to the Branch Technical Position, appendix A.II.B.

7.5 After curing 35 days in the controlled-temperature chamber and at room temperature as discussed in section 13.1 below, a total of three (3) cubes will be subjected to compressive strength testing per applicable steps of ASTM Standard C-109 and the applicable steps of ACM-4801.

7.6 After curing 42 days in the controlled-temperature chamber and at room temperature as discussed in section 13.1 below, a total of three (3) cubes will be subjected to compressive strength testing per applicable steps of ASTM Standard C-109 and the applicable steps of ACM-4801.

8.0 <u>THERMAL CYCLING</u>

8.1 The heating/cooling chamber shall conform to the description given in ASTM Standard B-553. The thermal cycling test shall be performed in accordance with ACM-6200.

8.2 Because ASTM Standard B-553 addresses thermal cycling of electroplated plastics, some modifications to the test method are required. Testing will be performed on "bare" (i.e., not in a container) cylinders.

8.3 After a cure time of at least 28 days, or longer, as identified in section 7 above, unbagged cylinders should be placed in the test chamber, and a series of thermal cycles shall be carried out in accordance with sections 5.4.1 through 5.4.4 of ASTM Standard B-553, with the additional provision that the specimens should be allowed to come to thermal equilibrium at the high (60 degrees C) and low (-40 degrees C) temperature limits. Thermal equilibrium should be confirmed by measurements of the centerline temperature of at least one (1) specimen per test group.

8.4 Three (3) cylinders should be subjected to the thermal cycling tests.

8.5 Following exposure of 30 thermal cycles, the cylinders should be examined visually, and found to be free of any evidence of significant cracking, spalling, or bulk disintegration. The specimens should be photographed at this time, as a record of the cylinder condition without assessing whether the defects are significant. Visible evidence of significant degradation would be indicative of a failure of the test.

8.6 If there are NO significant defects, the test cylinders shall be subjected to compressive strength testing per QIP-27 or ACM-4701 and applicable sections of ASTM Standard C-39. A mean compressive strength greater than 500 psi is desired.

8.7 Quality Assurance may perform a surveillance of the thermal cycling, inspection process, or compressive testing.

9.0 LEACH TESTING OF RADIONUCLIDES

9.1 For this test, a cylinder will be prepared in the A&PC Lab, using simulant "spiked" with Cesium-137, Strontium-90, and Plutonium-241.

9.2 After curing, the cylinder will be immersed in either deionized water or synthetic sea water for a period of 5 days, as discussed in the Branch Technical Position, appendix A.II.F.

9.3 The most aggressive leachant (deionized water vs. synthetic sea water) will be identified by performing 24-hour (or longer) leaching measurements on both leachants, and the leachant which exhibits the lowest leach index (highest leach rate) will be used for the remaining tests.

9.4 Leach testing will be performed in accordance with the Branch Technical Position, appendix A.II.F, and ANS/ANSI Procedure 16.1, and ACM-6300. The cylinder will be immersed in a measured volume of water, which is changed at intervals of 2, 7, 24, 48, 72, 90, and 120 hours. Upon removal of the cylinder (in accordance with ANSI/ANS 16.1, section 2.3) the leachant will be analyzed for Cesium-137, Strontium-90, and Plutonium-241 concentration. Each concentration is expressed as an "L" value for that leaching interval. The "L" value is the logarithm of the inverse of the effective diffusivity for each isotope. The "Leachability Index" is the arithmetic mean of the "L" values. The Leachability Index, as calculated in accordance with ANS/ANSI 16.1, should be greater than 6.0.

10.0 IMMERSION TESTING

10.1 No "Standard Method of Test" for immersion testing has been adopted for low-level radioactive waste. The test, however, is discussed in the Branch Technical Position, appendix A.II.G. and shall be performed in accordance with ACM-6400.

10.2 After a cure time of 28 days, or as indicated by the compressive strength vs. cure time testing performed in section 7.0 above, at least three (3) cylinders will be immersed for a period of 90 days.

10.3 The immersion liquid shall be either deionized water or synthetic sea water. The immersion liquid will be selected during the leach testing described in section 9.3 above.

10.4 Following immersion, the cylinders should be examined visually, and should be free of any evidence of cracking, spalling, or bulk disintegration. The specimens should be photographed at this time.

10.5 If there is no evidence of significant degradation, the specimens shall be subjected to compressive strength testing per QIP-27 or ACM-4701 and applicable sections of ASTM Standard C-39. Post-immersion mean compressive strengths should be greater than or equal to 500 psi, and not less than 75 percent of the pre-immersion (as-cured) mean compressive strength.

10.6 If the post-immersion mean compressive strength is less than 75 percent of the as-cured specimens' pre-immersion mean compressive strength, but not less than 500 psi, the immersion testing interval should be extended (using additional specimens) to a minimum of 180 days. For these cases, compressive strength testing should be conducted after 120, 150, and 180 days of immersion to establish that the compressive strengths level off and do not continue to decrease with time.

10.7 Quality Assurance may perform surveillance of the immersion, post-immersion inspection, and compressive strength testing processes.

11.0 LEACH TESTING FOR HEAVY METALS

11.1 One (1) cured sample specimen will be used for Toxicity Characteristic Leaching Procedure (TCLP) testing for Chromium.

11.2 A total of 100 grams of the sample material will be crushed and extracted in accordance with ACM-5901.

11.3 The resulting extract liquid will be analyzed for the presence of chromium.

11.4 A Chromium concentration less than the regulatory limit of 5.0 mg/l is required.

12.0 SAMPLING

12.1 Lab-scale (cube) samples will be produced in accordance with ACM-4701.

12.2 Full-scale cube and cylinder samples will be produced in accordance with SIP 91-01.

12.3 A total of forty (40) cubes and fifty (50) cylinders will be required in accordance with Table 1.

13.0 CURING

13.1 Lab-scale cube specimens, full-scale cube specimens, and full-scale cylindrical specimens will be cured, to the extent practical, at the same conditions as full-scale drums, as discussed in the Branch Technical Position, appendix A.III.B.

13.2 When processing full-scale drums under SIP 91-01, a drum will be equipped with thermocouples and a temperature recorder. The drum centerline temperature will be plotted as a function of time. This temperature profile will be duplicated, to the extent practical, for all samples cured outside of the drum.

13.3 For this procedure, the samples will be bagged and cured in a controlled-temperature chamber for a period of time equivalent to the peak hydration period. This period is taken to be that required for the drum centerline temperature to decrease to 30 degrees celsius.

13.4 The chamber will be equipped with a calibrated thermometer, and continuous temperature recorder.

13.5 All samples will be kept in sealed containers and/or poly bags during curing and storage, as discussed in the Branch Technical Position, appendix A.III.C. This is intended to simulate the environment in a sealed drum.

14.0 COMPRESSIVE STRENGTH TESTING OF CYLINDERS

14.1 The maximum practical compressive strength of the waste form will be evaluated as discussed in the Branch Technical Position, appendix A.II B.

14.2 Capping of cylindrical specimens shall be performed in accordance with the applicable steps of ASTM Standard C-39 and QIP-27.

14.3 Compressive strength testing of cylinders shall be performed in accordance with the applicable steps of ASTM Standard C-39 and QIP-27.

14.4 A minimum of ten (10) cylinders shall be tested.

14.5 A mean compressive strength in excess of 500 PSI is required.

14.6 Cylinders shall be bagged prior to compressive strength testing, in accordance with QIP-27.

TABLE 1

Sample Schedule for Qualification of the Nominal Recipe for Cement Solidification of Sludge Wash Liquids

Elapsed Days	Event	Cubes	Cylinders
0	Cast cubes/cylinders Begin cure	40	50
7	7-day compressive strength	3	3
14	14-day compressive strength	3	3
21	21-day compressive strength	3	3
28	28-day compressive strength	10	10
28	immersion starts	(BELOW)	(BELOW)
28	thermal cycling	-	4
28	TCLP	-	1
35	35-day compressive strength	3	3
42	42-day compressive strength	3	3
118	Post-immersion Compressive Strength	3	3
148	Post-immersion Compressive Strength	3	3
178	Post-immersion Compressive Strength	3	3
208	Post-immersion Compressive Strength	3	3
	TOTAL	37	42

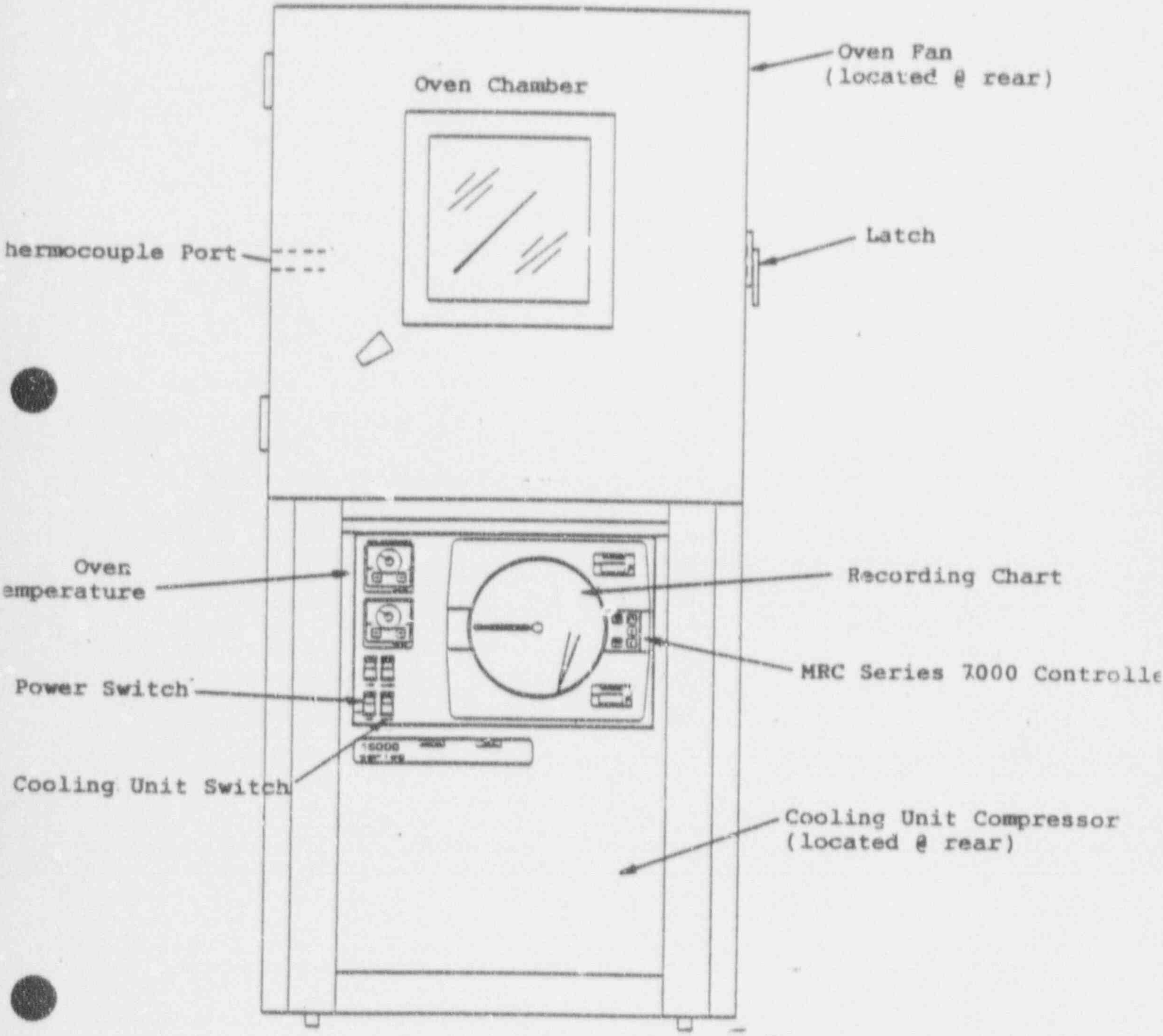
TABLE 2

Salt Concentrations for the "Nominal"
Simulant Recipe Based on 128.5" Heel

Constituent	Formula	Weight
Sodium Nitrate	$NaNO_3$	35.62
Sodium Nitrite	$NaNO_2$	33.84
Sodium Sulfate	Na_2SO_4	21.13
Sodium Bicarbonate	$NaHCO_3$	*
Potassium Nitrate	KNO_3	2.23
Sodium Carbonate	Na_2CO_3	6.02
Sodium Hydroxide	NaOH	0.22
Sodium Chromate	Na_2CrO_4	0.308
Sodium Chloride	NaC_1l	0.234
Sodium Phosphate	Na_3PO_4	0.190
Sodium Molybdate	Na_2MoO_4	0.040
Sodium Borate	$Na_2B_4O_7$	0.024
Citric Acid	$C_6H_8O_7$	0.032
Oxalic Acid	$C_2O_4H_2$	0.032
Tartaric Acid	$C_4H_6O_6$	0.032
Water	H_2O	203.03
	Total Weight	302.982
Weight of Solids		99.952
Weight Percent Solids		33%

* Note: Sodium Bicarbonate does not appear as $NaHCO_3$ at elevated pH

Figure 1: Despatch Series 16000 Environmental Chamber with MRC 7000 Controller



WEST VALLEY NUCLEAR SERVICES COMPANY

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WV-1008, Rev. 2
KMJ0040.WP3

TEST SUMMARY REPORT

Rev. 0

TEST/TEST SERIES Sludge Wash Cement Waste Form Qualification

DESCRIPTION Qualification Work with Cubes & Cylinders

TEST REQUEST NO. WVNS-TRQ-026 TEST PLAN NO. WVNS-TP-026

TEST COMMENCEMENT DATE 05/02/91 TEST COMPLETION DATE 08/27/91
Engineering Release #2272, Date 02/06/92

1.0 OBSERVATIONS/COMMENTS

The purpose of this test procedure was to perform qualification work on cement waste forms simulating the cement waste to be generated following sludge washing. The test procedure is partially complete and a future revision to this Test Summary Report will be issued to incorporate the results of immersion and TCLP-Cr tests. The individual objectives defined in the Test Request are reviewed in section 3.0.

2.0 REFERENCES

1) TE-WVNS-TRQ-026-001 Test Exception change of nominal recipe listed in TRQ-026, 5-28-91, M. N. Baker

2) TE-WVNS-TRQ-026-002 Test Exception change of spike simulant for leachant selection testing, 5-29-91, J. L. Mahoney

3) TE-WVNS-TP-026-001 Test Exception change of curing time and temperature for cubes & cylinders, 5-13-91, M. N. Baker

4) TE-WVNS-TP-026-002 Test Exception change of nominal recipe listed in TP-026, 5-28-91, M. N. Baker

5) TE-WVNS-TP-026-003 Test Exception change of spike simulant for leachant selection testirg, 5-29-91, J. L. Mahoney

6) TE-WVNS-TP-026-004 Test Exception substitution of an undersized cube for compressive strength measurement with another cube, 6-6-91, M. N. Baker

7) Letter FH:91:0107, L. E. Michnik to J. L. Mahoney, "15-day Summary of Work Performed for WVNS-TRQ-026", dated May 8, 1991

8) WVNS-SIP-91-01, "LWTS/CSS Integrated Test", May 2, 1991 including Test Exceptions TE-WVNS-SIP-91-01-001 through TE-WVNS-SIP-91-01-009.

9) United States Nuclear Regulatory Commission "Technical Position on Waste Form" Revision 1, January, 1991.

3.0 CONCLUSIONS/ACCEPTABILITY OF RESULTS/OBJECTIVES MET

The acceptability of results of the six objectives from WVNS-TRQ-026 are presented below.

3.1 Compressive Strength vs Cure Time (objective 2.1)

Activity

Determine the compressive strength of both cubes and cylinders as a function of cure time. Identify a cure time that achieves a strength of 75% of the peak compressive strength.

Task Accomplished

This task was completed. During the LWTS/CSS Integrated Test Run, twenty batches of cement waste were sampled (SIP-91-01). During the sampling, cube forms and cylinder forms were filled with cement product. The filled forms were inserted into a controlled temperature chamber for curing at 79 ± 2°C for a total of 90 -0/+8 hours (TP-026). Following this high-temperature cure, the cubes and cylinders were allowed to finish their curing at room temperature. At pre-defined days, a minimum of three cubes and cylinders were crushed. After a minimum of four weeks, core samples were taken from several full-scale drums (TP-030) for crushing. Compressive strength data for cubes, cylinders, and cores are presented in Table 1. Figures 1, 2, and 3 indicate the time-dependent nature of the compressive strength measurements.

Statistical comparisons indicate the cube compressive strength measurements up through 21 days of curing can be proven to be from a different population than the strengths from 27 days and beyond (Appendix A). Cured strength values need to be differentiated from those samples that are not fully cured. This statistical comparison indicates that any sample cured for at least 27 days can be considered fully cured. The pre-cured average compressive strength for cubes is 844 psi. The average cured strength is 1046 ± 80 psi (at 95% confidence of the mean). A Chi-Square test of the distribution of compressive strength values for all data from 27 days and beyond show the measurements to be normally distributed (Appendix B). For cubes, the 75% of peak compressive strength value is 784 psi which is achieved within the first 7 days of curing.

For cylinder data, statistical comparisons indicate the compressive strength measurements up through only 8 days of curing can be proven to be from a different population than the strengths from 15 days and beyond (Appendix A). The pre-cured average compressive strength for cylinders is 1118 psi. The average cured strength is 1284 ± 62 psi (at 95% confidence of the mean). A Chi-Square test of the distribution of compressive strength values for all data from 15 days and beyond show the measurements to be normally distributed (Appendix B). For cylinders, the 75% of peak compressive strength value is 963 psi which is also achieved within the first 7 days of curing.

A cross-plot of compressive strength measurements of cylinders versus those for cubes (both made from the same cement batch in CSS) is shown in Figure 4. The scatter (correlation coefficient = 0.01) shows no correlation between the measurements. This indicates that the uncertainties in both compressive strength measurements dominate the range of data.

3.2 Compressive Strength After 28 Days (objective 2.2)

Activity

Verify the compressive strength of the cement product is greater than 500 psi after a minimum of 28 days of curing.

Task Accomplished

As noted above, the mean compressive strength for both cubes and cylinders was greater than 500 psi as early as 7 days of curing. After 28 days of curing the strengths remained above 500 psi.

3.3 Thermal Cycling Stability (objective 2.3)

Activity

Complete a thermal cycling stability test per the US NRC "Technical Position on Waste Form" and the ASTM standard B-553. Confirm that the mean compressive strength is greater than 500 psi and that no significant cracking, spalling, or disintegration of the specimens occurred.

Task Accomplished

After curing for 49 days, three cylinders and one instrumented cylinder were placed into a controlled temperature chamber. The temperature was cycled from 60°C to 20°C to -40°C and back with one hour soak periods at each temperature. Thirty of these temperature cycles were completed on the cylinders. Compressive strength data is presented in Table 2.

Statistically, the compressive strength of the cylinders that were thermally cycled cannot be distinguished from cured cylinders. The average for the cycled cylinders is 1229 psi versus the cured cylinder mean of 1284 ± 62 psi. No cracking, spalling, or disintegration of the test specimens were detected.

3.4 Leachant Selection (objective 2.4)

Activity

Complete measurements of the resistance to both deionized water and synthetic sea water per the US NRC "Technical Position on Waste Form" and the ANS/ANSI procedure 16.1. Identify the more aggressive leachant for immersion tests. Confirm the waste form has a leachability index (per ANS/ANSI procedure 16.1) greater than 6.0.

Task Accomplished

Cement-waste mini-cylinders (1" diameter x 3" height) were fabricated from spiked decontaminated supernate. Samples of decontaminated supernate were collected in the laboratory. These combined solutions were spiked with additional sodium sulfate and pH adjusted to 11.8 to simulate sludge wash solutions. By using chemically adjusted supernate, the levels and chemical states of the key radionuclides of interest were preserved.

Table 3 lists the calculated leach indices (per ANS/ANSI procedure 16.1) at intervals from 2 to 120 hours for Tc-99, Sr-90, Cs-137, and alpha Pu in both demineralized water and synthetic sea water. All indices are over 6.0 showing the waste form meets its leaching criteria. The data are also plotted in Figures 5 and 6. Technetium was the species leached most rapidly (lowest leach index).

The nominal more aggressive leachant varied with time and radionuclide. Although Table 3 lists the nominal more aggressive leachant, a statistical comparison of the two for Tc-99 shows almost no discernable difference.

Table 4 lists the triplicate measurements that are the source of the averages listed in Table 3. The second portion of Table 4 performs the comparison of differences between demineralized water and synthetic sea water. A significance level (see Appendix A for the equation to determine the significance level) is calculated based on the comparison of the two sets of measurements.

For the time marks of 2, 24, 72, and 96 hours, demineralized water and synthetic sea water were equally aggressive on the cement waste form. At 7 hours, demineralized water was more aggressive. Synthetic sea water was more aggressive at the 48 and 120 hour mark. Overall the two leachants were deemed to be equally aggressive thus demineralized water would be used for the immersion tests.

3.5 Immersion Testing (objective 2.5)

Activity

Following leachant selection tests, perform immersion testing of the cement waste form for a minimum of 90 days or up to 180 days. Compressive strengths of the immersed waste forms shall be compared to the cured average prior to immersion per the US NRC Branch Technical Position paper. Confirm that the test specimens show compressive strengths greater than 75% of the average cured pre-immersion strength after 90 days of immersion. If strength values are below 75%, confirm that the immersed strength levels off above 500 psi after 180 days of immersion. In either case, also confirm that the test specimens show no significant cracking, spalling, or bulk disintegration.

Task Accomplished

This task remains open. The immersion tests are underway in demineralized water. Compressive strength measurements will be collected and compared to the cured average per the US NRC paper.

3.6 TCLP-Cr Testing (objective 2.6)

Activity

Complete a standard Toxicity Characteristics Leaching Procedure (TCLP) test for chromium on a waste form produced during the LWTS/CSS Integrated Test Run. Confirm the test specimens yield < 5 ppm Cr in the leachant.

Task Accomplished

This task remains open. A cube produced from cement waste collected during the LWTS/CSS Integrated Test Run was extracted for chromium on July 23, 1991. Per the test procedure, the extract must be analyzed for Cr within 180 days. Following analysis, the data will be presented in a revision to this test summary.

4.0 ACTIONS OUTSTANDING

Desired activities and analyses that remain as of this writing are outlined below:

4.1 Immersion Testing (objective 2.5)

Complete compressive strength measurements of the immersed waste forms for up to 180 days from start of immersion. Compare the waste form compressive strengths to those of the unimmersed cured waste.

Action: Analytical & Process Chemistry
Timing: January 15, 1992

4.2 TCLP-Cr Testing (objective 2.6)

Per the TCLP procedure, complete the chromium measurement of the cement waste form extract.

Action: Analytical & Process Chemistry
Timing: January 24, 1992

4.3 Revise the Test Summary Report

Update the TSR to reflect results from both the immersion tests and TCLP-Cr tests.

Action: IRTS Engineering
Timing: March 1, 1992

APPROVAL(S) ______________ ADDITIONAL REVIEWERS: YES NO
J. L. Mahoney

M. N. Baker

A. J. Howell

L. E. Michnik

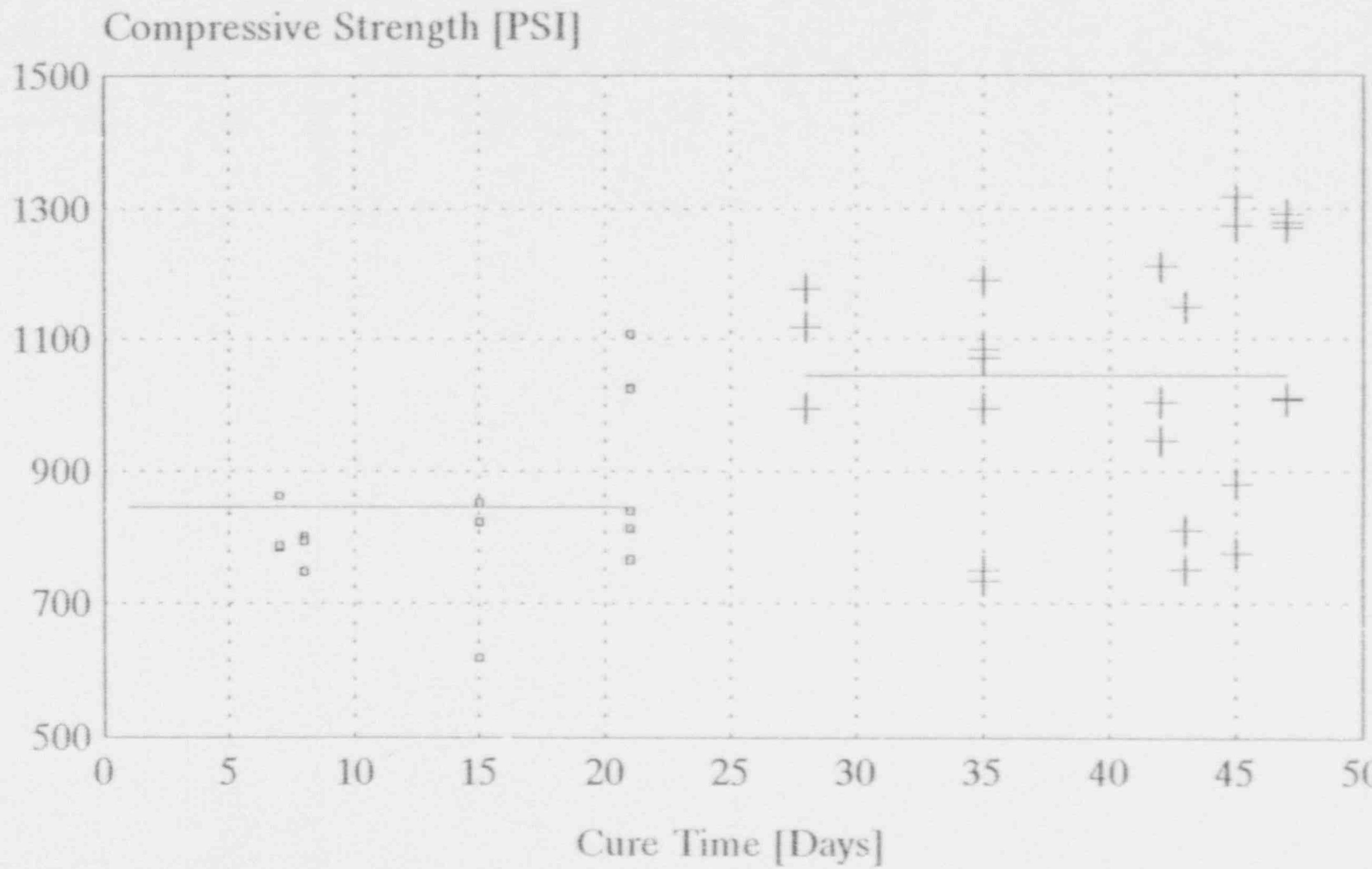
D. C. Meess

Quality Assurance

Table 1
Compressive Strength of Cubes, Cylinders, & Cores

Days	Cubes PSI	Cubes Drum	Cyl PSI	Cyl Drum	Core PSI	Core Drum	Days
7	785	81438	1111	81438			
7	862	81632	1188	81632			
7	789	81653	1026	81653			
8	749	81299	934	81299			
8	802	81408	1082	81408			
8	795	81420	1365	81420			
15	823	81300	1493	81301			
15	851	81438	1408	81438			
15	519	81439	1514	81439			
21	767	81265	1231	81265			
21	839	81298	1203	81298			
21	1025	81406	1125	81406			
21	1108	81416	1394	81416			
21	813	81439	1344	81439			
21	1027	81632	1323	81440			
28	1119	81298	1500	81298	1120	81632	28
28	1177	81433	1358	81433			
28	996	81439	1464	81439			
35	750	81294	1252	81294	1204	81632	35
35	1084	81296	1337	81296			
35	995	81300	1096	81300			
35	1189	81301	1337	81301			
35	735	81408	828	81408	1389	81632	42
35	1071	81632	1217	81632	1431	81632	42
42	1005	81263	1698	81263	1305	81632	42
42	1210	81440	1239	81440	1215	81300	43
42	946	81653	1004	81653	1199	81300	43
43	752	81418	1549	81418	909	81300	43
43	810	81433	1436	81433	1296	81300	43
43	1149	81438	1075	81438	1279	81439	45
45	1317	81263	1210	81263	1086	81439	45
45	1274	81418	1337	81418	883	81439	45
45	881	81418	1252	81418	1389	81414	47
45	776	81433	1181	81433	1431	81414	47
47	1011	81296	1153	81296	1215	81420	48
47	1291	81299	1287	81299	1360	81420	48
47	1008	81414	1153	81414	1191	81439	49
47	1271	81416	1217	81416	1328	81439	49
47	1279	81420	1125	81420	1441	81439	49

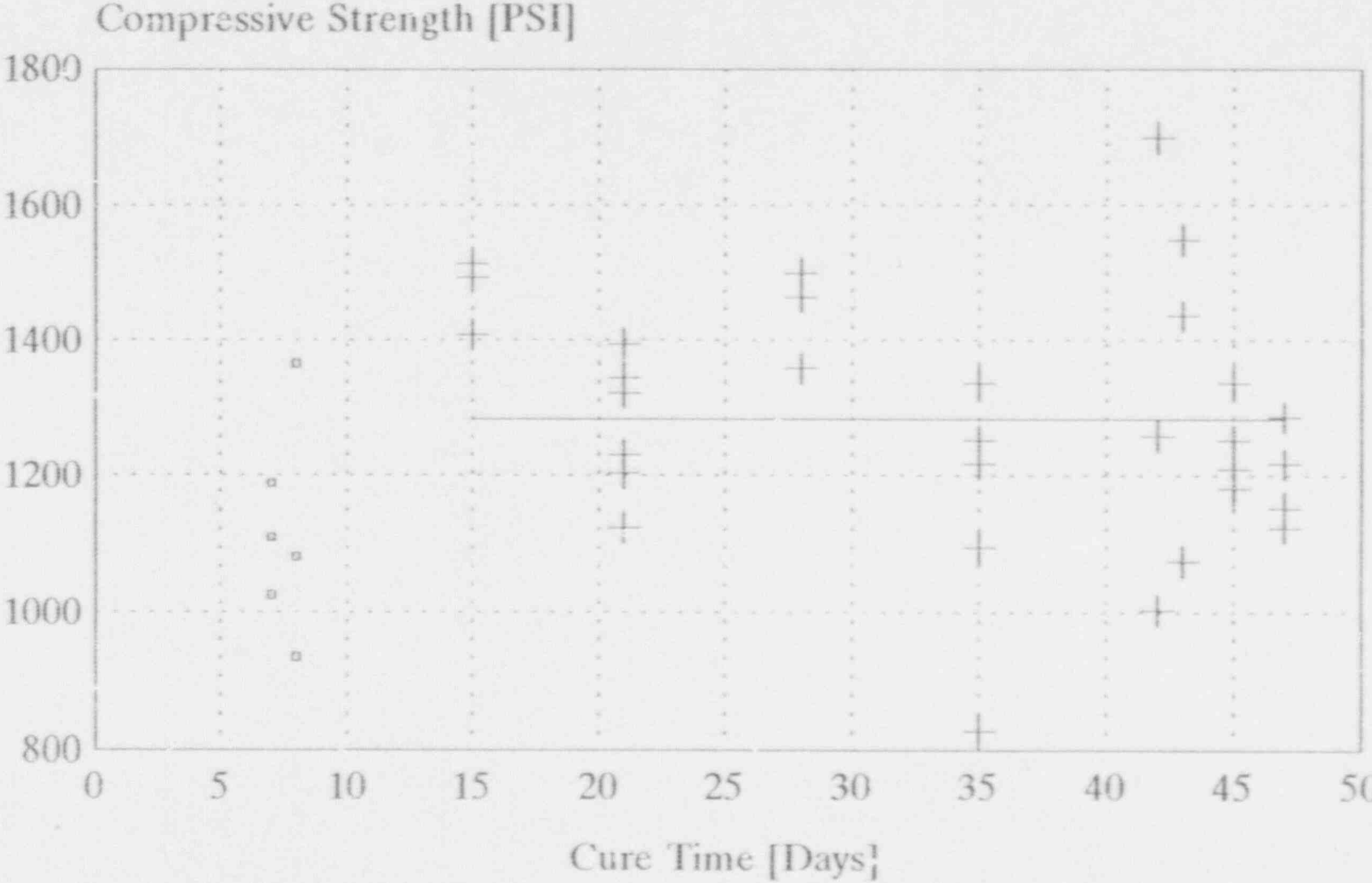
Compressive Strength Analysis TP-026
2" Cubes Strength vs Curing Time



Avg pre-cured: 844 psi
Avg cured: 1046 psi

Figure 1

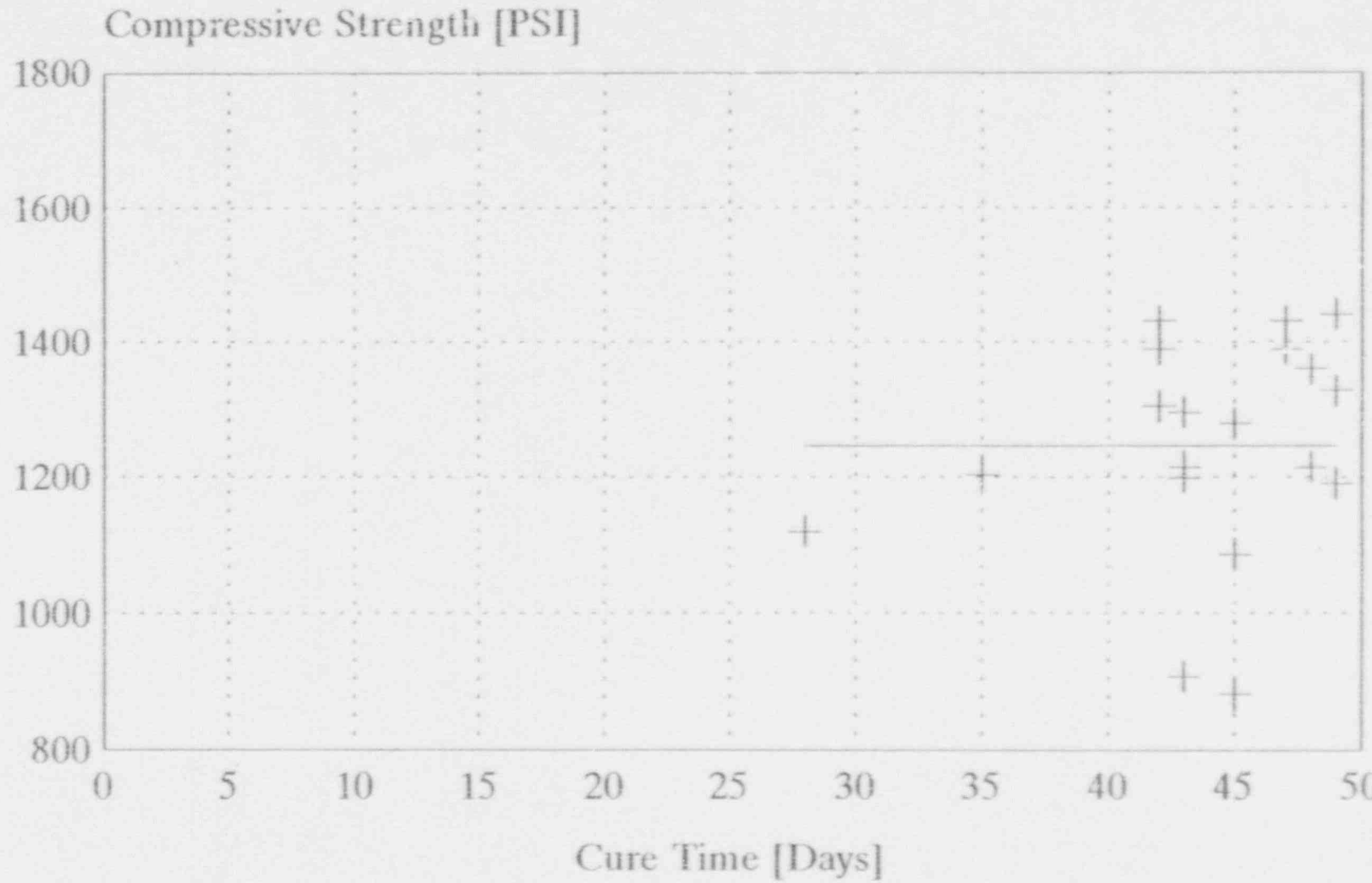
Compressive Strength Analysis TP-026
Cylinder Strength vs Curing Time



Avg cured: 1284 ± 62 psi

Figure 2

Compressive Strength Analysis TP-026
Core Strength vs Curing Time



Avg cured: 1246 ± 78 psi

Figure 3

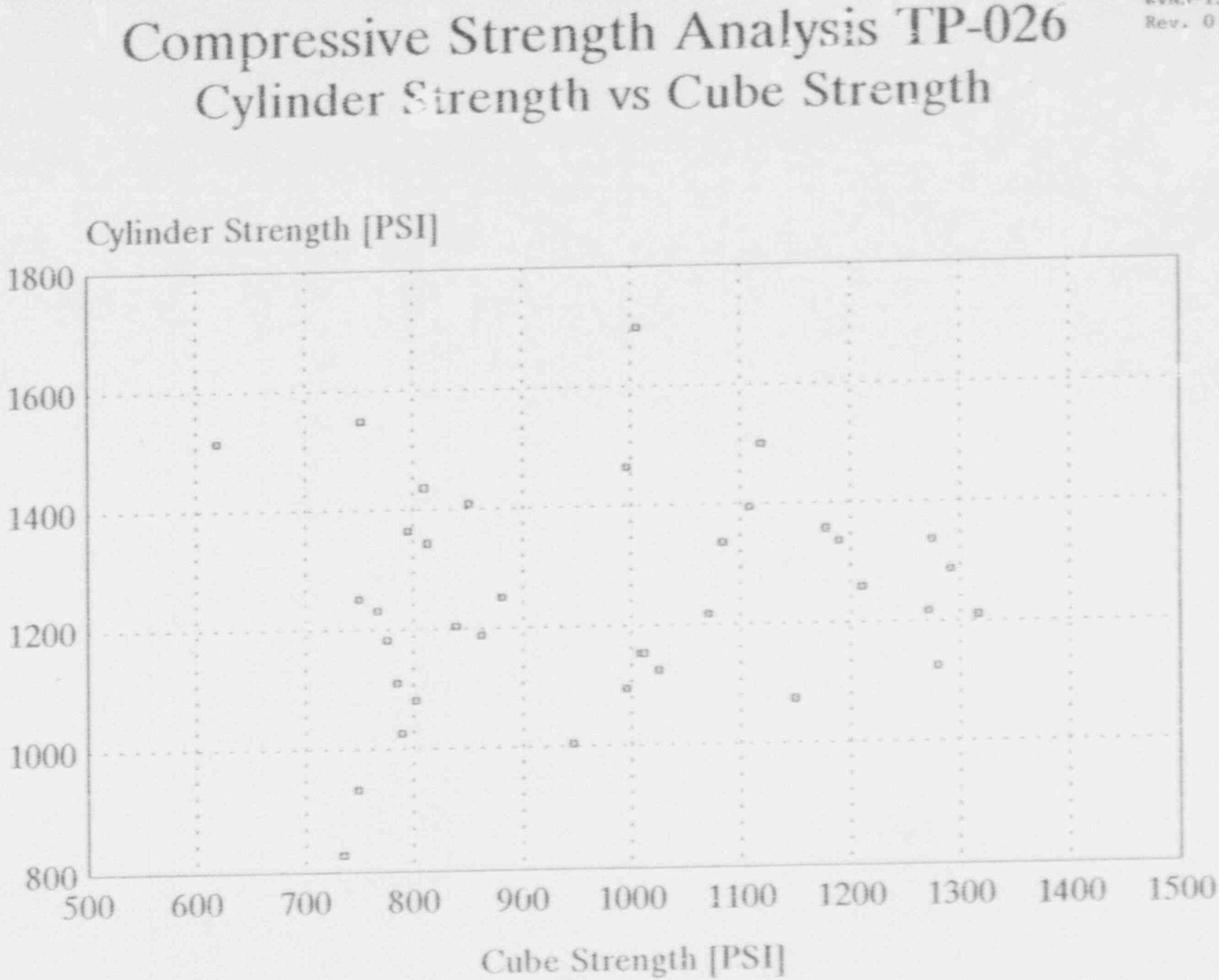

Compressive Strength Analysis TP-026
Cylinder Strength vs Cube Strength
Cylinder Strength [PSI]
1800
1600
1400
1200
1000
800
500
600
700
800
900
1000
1100
1200
1300
1400
1500
Cube Strength [PSI]

Figure 4

Table 2
Compressive Strength of Thermal-Cycled Cylinders

Drum	Compressive Strength [PSI]
81294	1079
81296	1324
81414	1283

Table 3
Leachant Selection Testing Results

In Demineralized Water
Average Leachability Index

hrs	Tc-99	Sr-90	Cs-137	α Pu
2	7.725	10.026	7.813	14.047
7	7.831	9.974	8.051	14.219
24	7.692	10.08	7.976	14.224
48	8.112	10.355	8.457	12.962
72	8.555	10.895	8.91	13.083
96	8.936	10.985	9.324	13.186
120	9.299	11.313	9.681	13.269

In Synthetic Sea Water
Average Leachability Index

hrs	Tc-99	Sr-90	Cs-137	α Pu
2	7.885	10.424	7.977	11.751
7	8.010	10.726	8.289	11.924
24	7.797	11.392	8.060	13.235
48	8.026	10.85	8.393	11.153
72	8.459	10.637	8.847	11.682
96	8.879	11.509	9.225	11.783
120	9.138	11.783	9.598	12.106

More Aggressive Leachant

hrs	Tc-99	Sr-90	Cs-137	α Pu
2	Demin	Demin	Demin	Sea
7	Demin	Demin	Demin	Sea
24	Demin	Demin	Demin	Sea
48	Sea	Demin	Sea	Sea
72	Sea	Sea	Sea	Sea
96	Sea	Demin	Sea	Sea
120	Sea	Demin	Sea	Sea

Leachability Indicies TP-026
Demineralized Water

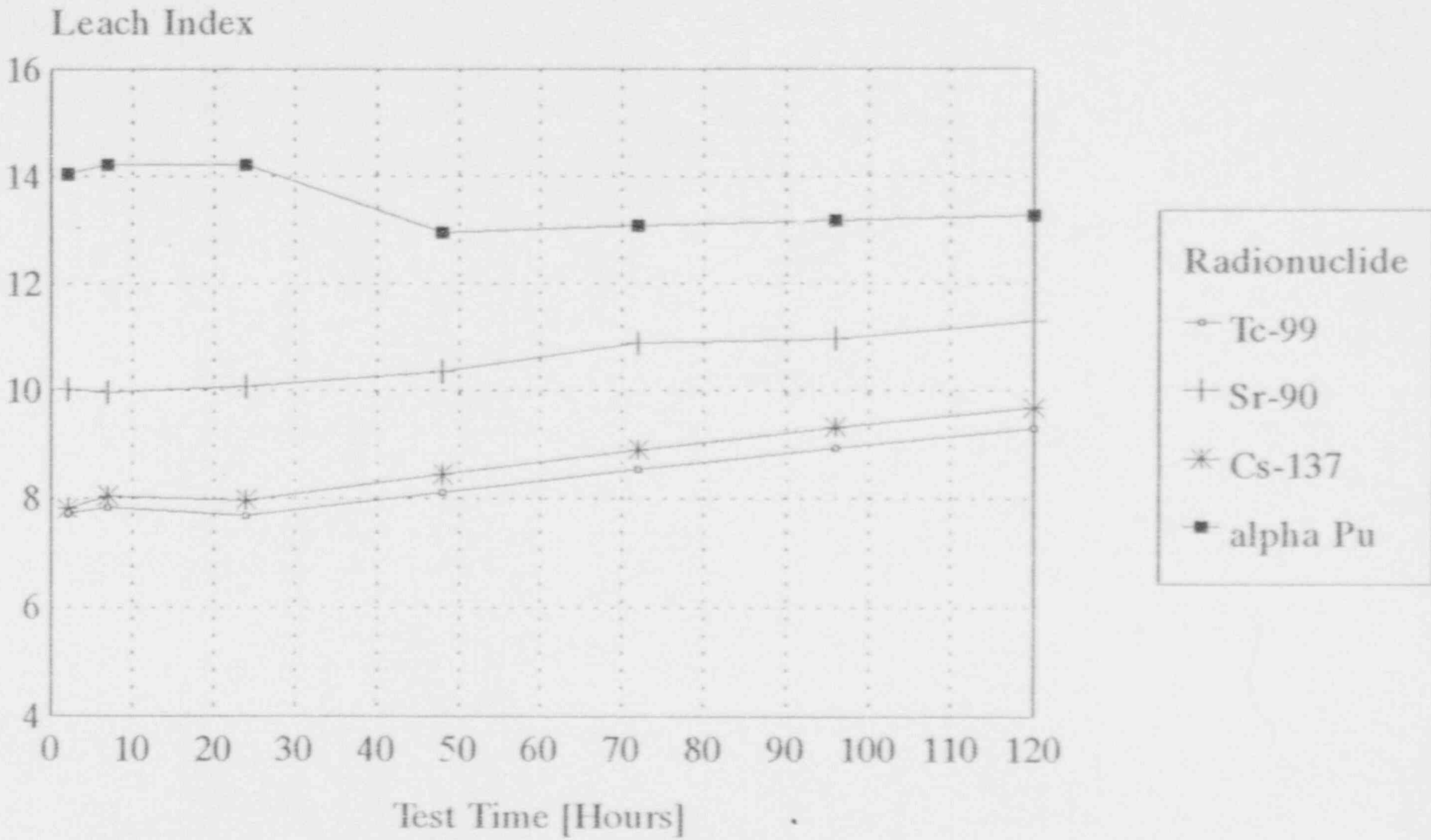


Figure 5

Leachability Indicies TP-026
Synthetic Sea Water

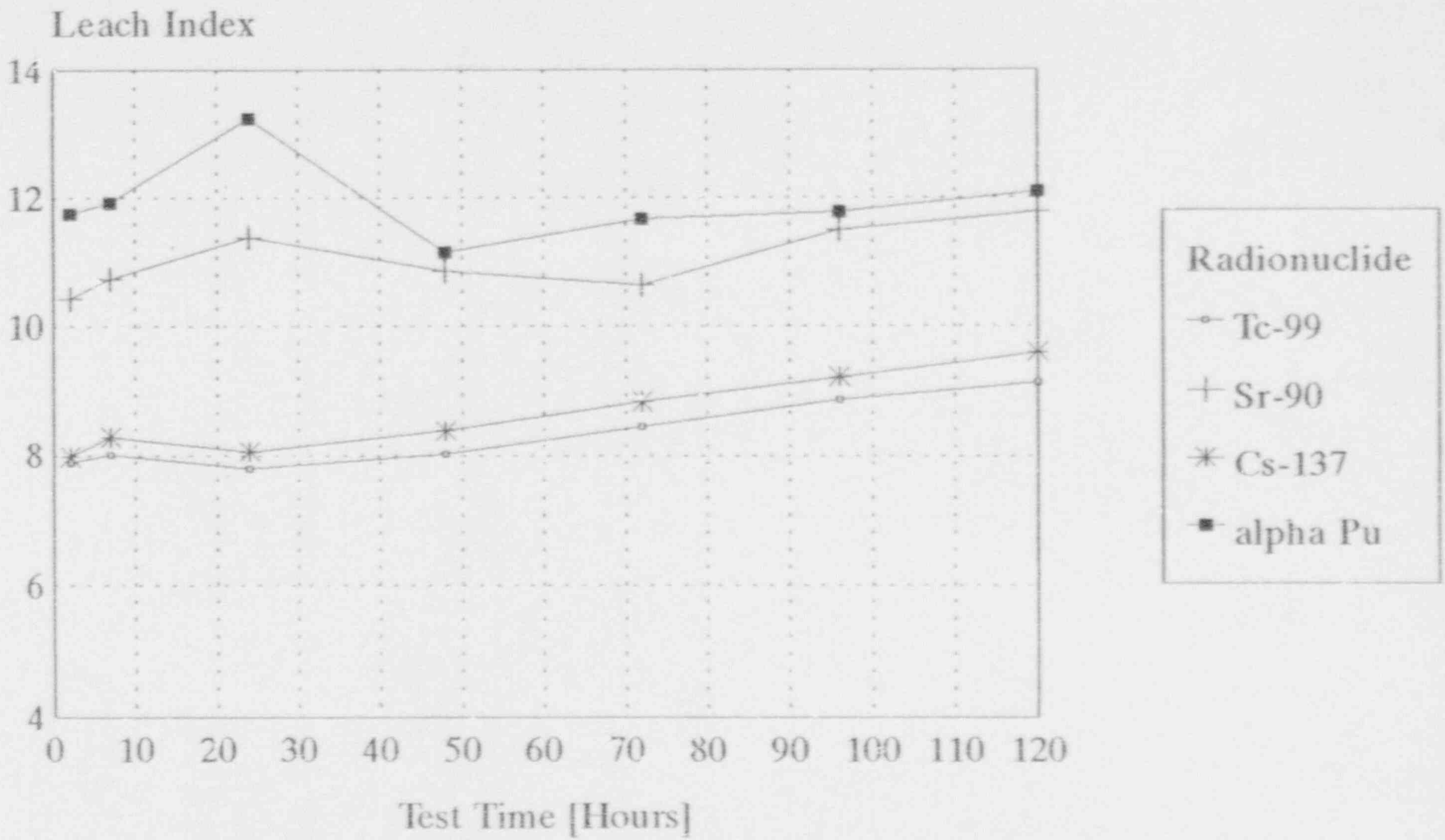


Figure 6

Table 4

Statistical Comparison of Leach Indices for Tc-99

Leach Indices
Triplicate Measurements for Tc-99

hrs	Demineralized Water			Synthetic Sea Water		
2	7.716	7.74[illegible]	7.718	8.091	7.781	7.785
7	7.894	7.782	7.816	8.016	7.991	8.024
24	7.765	7.640	7.672	7.815	7.781	7.794
48	8.074	8.122	8.141	7.985	8.053	8.040
72	8.588	8.490	8.587	8.430	8.508	8.439
96	8.919	8.954	---	8.892	8.866	---
120	9.246	9.280	9.370	9.170	9.131	9.114

Statistical Comparison of Leach Indices for Tc-99

	Demin Water		Synth Sea Water			Signif	
hrs	Avg	Var	Avg	Var	Delta	Level	Diff?
2	7.73	0.00015	7.89	0.02108	0.16	0.29	No
7	7.83	0.00220	8.01	0.00020	0.18	0.10	Yes
24	7.69	0.00281	7.80	0.00020	0.10	0.11	No
48	8.11	0.00079	8.03	0.00087	0.09	0.08	Yes
72	8.56	0.00211	8.46	0.00121	0.10	0.11	No
96	8.94	0.00051	8.88	0.00017	0.06	0.07	No
120	9.30	0.00274	9.14	0.00055	0.16	0.11	Yes

Appendix A

Statistical Comparison of Compressive Strengths
Pre-Cured Versus Cured Strengths for Cubes

Days	PSI		Days	PSI
7	785	844 average	28	1119
7	862	14266 variance	28	1177
7	789	15 no. points	28	996
8	749		35	750
8	802		35	1084
8	795		35	995
15	823		35	1189
15	851		35	735
15	619		35	1071
21	767		42	1005
21	839		42	1210
21	1025		42	946
21	1108		43	752
21	813		43	810
21	1027		43	1149
		1046 average	45	1317
		34122 variance	45	1274
		24 no. points	45	881
			45	776
			47	1011
			47	1291
			47	1008
			47	1271
			47	1279

Delta between group averages = 202

Significant delta = $(var_1 * n_1 + var_2 * n_2)/(n_1 + n_2 - 2) *$
$(n_1 + n_2)/n_1/n_2)$^0.5*t-statistic

var_1, var_2 :	variance of the two groups
n_1, n_2 :	number of data points in each group
t-statistic:	from standard tables for 95% confidence with $n_1 + n_2 - 2$ degrees of freedom

Significant delta = 111

Delta between group averages > significant delta, therefore, the two groups are significantly different.

Appendix A (Cont.)

Statistical Comparison of Compressive Strengths
Pre-Cured Versus Cured Strengths for Cylinders

Days	PSI		
7	1111	1118	average
7	1188	18262	variance
7	1026	6	no. points
8	934		
8	1082		
8	1365		

		Days	PSI
		15	1493
		15	1408
		15	1514
		21	1231
		21	1203
		21	1125
		21	1394
		21	1344
		21	1323
		28	1500
		28	1358
		28	1464
		35	1252
		35	1337
		35	1096
1284	average	35	1337
29522	variance	35	828
33	no. points	35	1217
		42	1698
		42	1259
		42	1004
		43	1549
		43	1436
		43	1075
		45	1210
		45	1337
		45	1252

Delta between groups = 166

Significant delta = 154

Delta between groups > significant delta, therefore, the two groups are significantly different.

Appendix B

Chi-Square Test of Compressive Strength Data for Cubes

Sorted Strengths		Z value	Area	Qty Expected	Actual Qty	Error in group
		-infin	0			
735						
750						
752	group 1			3.5	5	0.67
776						
810						
avg break	845.5	-1.06	0.1446			
881						
946						
995	group 2			6.5	5	0.36
996						
1005						
avg break	1006.5	-0.21	0.4168			
1008						
1011						
1071	group 3			6.3	5	0.28
1084						
1119						
avg break	1134	0.47	0.6808			
1149						
1177						
1189						
1210						
1271						
1274	oup 4			7.7	9	0.23
1279						
1291						
1317						
		+infin	1			

Total group errors 1.55
95% significance Chi Square Value 3.84
Conclusion: Normal Gaussian Distribution

Appendix B (Cont)

Chi-Square Test of Compressive Strength Data for Cylinders

Sorted Strengths		Z value	Area	Qty Expected	Actual Qty	Error in group
		-infin	0			
828						
1004						
1075						
1096	group 1			6.7	6	0.07
1125						
1125						
avg break	1139	-0.83	0.2033			
1153						
1153						
1181	group 2			4.7	5	0.02
1203						
1210						
avg break	1213.5	-0.40	0.3446			
1217						
1217						
1231	group 3			3.0	5	1.28
1252						
1252						
avg break	1255.5	-0.16	0.4364			
1259						
1287						
1323						
1337	group 4			6.4	6	0.02
1337						
1337						
avg break	1340.5	0.33	0.6293			
1344						
1358						
1394	group 5			6.6	5	0.38
1408						
1436						
avg break	1450	0.95	0.8289			
1464						
1493						
1500						
1514	group 6			5.6	6	0.02
1549						
1698						
		+infin	1			

Total group errors 1.81
95% significance Chi Square Value 7.84
Conclusion: Normal Gaussian Distribution

West Valley Demonstration Project

Doc. Number WVNS-TRQ-028

Revision Number 1

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Engineering Release #2055
Per ECN #4388

TEST REQUEST

DEVELOPMENT OF THE PROCESS CONTROL PARAMETERS FOR
CEMENT SOLIDIFICATION OF SLUDGE WASH LIQUIDS

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RECORD OF REVISION

PROCEDURE

If there are changes to the procedure, the revision number increases by one. These changes are indicated in the left margin of the body by an arrow (>) at the beginning of the paragraph that contains a change.

Example:

> The arrow in the margin indicates a change.

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0	Original Issue	All	04/91
1	Per ECN #4388	All	07/01/91

RECORD OF REVISION (CONTINUATION SHEET)

Rev. No.	Description of Changes	Revision on Page(s)	Dated

DEVELOPMENT OF THE PROCESS CONTROL PARAMETERS FOR CEMENT SOLIDIFICATION OF SLUDGE WASH LIQUIDS

1.0 INTRODUCTION

1.1 This work is required to demonstrate the stability of the waste form at variable cement recipe and waste parameters. The characteristics which will be tested are required by 10 CFR 61, Code of Federal Regulations, Title 10, "Licensing Requirements for Land Disposal of Radioactive Waste," and the USNRC Branch Technical Position on Waste Form, Revision 1, draft dated December 1990.

1.2 Work will be performed with a simulant representing the actual waste liquid.

1.3 Work will be performed using 2" x 2" x 2" cubes prepared in the A&PC Laboratory.

1.4 Work will include the formulation of a series of solutions representing variations in the waste liquid, which will be mixed with the cement blend and other additives. The effect of variations in additives will also be evaluated, as discussed in the Branch Technical Position, Appendices A.V. and A. VI.

> 1.5 A screening test set as well as a multi-variant test set will be performed. The test matrices are shown in Tables 1 and 2.

1.6 Test Procedure WVNS-TP-028, providing instructions for testing in accordance with this Test Request shall be issued by Analytical & Process Chemistry per EP-11-003.

1.7 A Test Summary Report documenting the results of this testing shall be issued by the Cognizant Test Engineer per EP-11-003.

2.0 OBJECTIVES

> 2.1 Screening Tests

Thirteen variables will be varied from low (indicated by "-" in Table 1) to high (indicated by "+" in Table 2) as part of a Plackett-Burman-type 28-run screening experiment. The thirteen variables are listed below with applicable low and high values (ratios, i.e. 0.5x, are relative to the nominal LWTS concentrates recipe in Table 3, or cement recipe in Table 4):

>

variable	number	low	high
sulfate	1	0.5x	2x
nitrate:nitrite ratio	2	0.5	2.8
organics	3	0.5x	4x
aluminum (gm Al/gm Cl)	4	0	2.5
total solids (TDS)	5	25	37
water:cement ratio	6	0.3	0.8
calcium nitrate	7	0.5x	2x
pH	8	11	13
mix time (mins)	9	4	16
anti-foam	10	0.3x	2x
sodium silicate	11	0.5x	2x
phosphate (gm PO4/gm Cl)	12	0.01	7.0
boron (gm B/gm Cl)	13	0.001	0.15

Following compressive strength crushing of the cement cubes, data reduction will be mandatory by the Cognizant Test Engineer and Cognizant A&PC Scientist. The data reduction will identify key process variables (variances statistically significant compared to pooled variance) which will be varied in the multi-variant testing in the next section.

> 2.2 Multi-variant Testing

The multi-variant response of cement compressive strength will be evaluated via a Box-Behnken test. A two-set, five-variable Box-Behnken design is presented in Table 2. This type of experiment will provide response surface coefficients which cover all single variable and quadratic terms.

Before proceeding with this section of the test, an agreement will be reached between the Cognizant Test Engineer and Cognizant Scientist. This agreement will be documented in the form of a Test Exception (TE) to Test Procedure (WVNS-TP-028) per EP-11-003. The TE will define the number of variables in the study and the ranges to be evaluated in the test (in Table 2 high amounts are noted as "+1", low amounts are noted as "-1", and nominal values are noted as "0").

3.0 SAFETY

3.1 Industrial safety practices shall be as described in the WVNS Hygiene & Safety Manual, WVDP-011.

3.2 Radiological work will be performed in accordance with the WVDP Radiological Controls Manual, WVDP-010.

3.3 Safety practices specific to the A&PC Laboratory will be as described in ACP 7.2, Safety Practices for the Analytical & Process Chemistry Department.

4.0 EQUIPMENT CONFIGURATION

4.1 All lab equipment will be set up in accordance with Test Procedure WVNS-TP-028 as directed by the Cognizant A&PC scientist or Cognizant A&PC technician.

4.2 Balances and other weighing equipment accurate to 0.01 gram will be calibrated prior to use in accordance with ACP-7.1.

4.3 Mixing will be performed in a manner which duplicates, to the extent practical, the full-scale mixing equipment, including mixing speed, order of addition, mixing time, energy introduced to the mixture, etc., as discussed in the Branch Technical Position, appendix A.III.A.

4.4 Curing of the samples will be performed in a manner which duplicates, to the extent practical, the curing temperature profile encountered in the full-scale drum, as discussed in the Branch Technical Position, appendix A.III.B. A temperature-controlled chamber will be utilized.

4.5 Calibration of compressive strength testing equipment will be in accordance with ASTM Method C-39 and C-109.

5.0 SAMPLING

5.1 Samples will be produced in the quantities and frequencies specified in WVNS-TP-028.

> 5.2 The test matricies are shown in Tables 1 and 2. Each test will be conducted with the variables adjusted to the maximum (shown by a "+" or "+1"), the nominal value (shown by a "0"), or the minimum value (shown by a "-" or "-1"). Independent as well as dependent variables will be evaluated.

6.0 PERSONNEL QUALIFICATION

6.1 Testing will be performed by qualified Analytical & Process Chemistry Technicians using WVNS-TP-028 and approved Analytical Chemistry Methods (ACM's) under the cognizance of an A&PC scientist.

a. Radiochemistry "B" Technicians qualified to WVNS-QS-014

b. Radiochemistry "A" Technicians qualified to WVNS-QS-016

>

Table 1

TWENTY-EIGHT-RUN PLACKETT-BURMAN SCREENING DESIGN

Note: Before running tests, the order shall be randomized

	Variable Number												
Trial	1	2	3	4	5	6	7	8	9	10	11	12	13
1	+	-	+	+	+	+	-	-	-	-	+	-	-
2	+	+	-	+	+	+	-	-	-	-	-	+	+
3	-	+	+	+	+	+	-	-	-	+	-	-	-
4	-	-	-	+	-	+	+	+	+	-	-	+	-
5	-	-	-	+	+	-	+	+	+	+	-	-	-
6	-	-	-	-	+	+	+	+	+	-	+	-	+
7	+	+	+	-	-	-	+	-	+	-	-	+	-
8	+	+	+	-	-	-	+	+	-	+	-	-	+
9	+	+	+	-	-	-	-	+	+	-	+	-	-
10	-	+	-	-	-	+	-	-	+	+	+	-	+
11	-	-	+	+	-	-	+	-	-	-	+	+	+
12	+	-	-	-	+	-	-	+	-	+	-	+	-
13	-	-	+	-	+	-	-	-	+	+	-	+	+
14	+	-	-	-	-	+	+	-	-	+	+	-	-
15	-	+	-	+	-	-	-	+	-	-	+	+	+
16	-	-	+	-	-	+	-	+	-	+	-	+	+
17	+	-	-	+	-	-	-	-	+	+	+	-	+
18	-	+	-	-	+	-	+	-	-	-	+	+	-
19	+	+	-	+	-	+	+	-	+	+	-	+	+
20	-	+	+	+	+	-	+	+	-	+	+	-	+
21	+	-	+	-	+	+	-	+	+	-	+	+	+
22	+	-	+	+	+	-	+	-	+	-	-	-	+
23	+	+	-	-	+	+	+	+	-	-	-	-	+
24	-	+	+	+	-	+	-	+	+	-	-	-	-
25	+	-	+	+	-	+	+	+	-	+	+	+	-
26	+	+	-	+	+	-	-	+	+	+	+	+	-
27	-	+	+	-	+	+	+	-	+	+	+	+	-
28	-	-	-	-	-	-	-	-	-	-	-	-	-

Table 2

TWO-SET, FIVE VARIABLE BOX-BEHNKEN TEST DESIGN

Note: Before running tests, the order in each set shall be randomized, but the sets shall not be mixed.

	Variable Number				
Trial	1	2	3	4	5
1	+1	+1	0	0	0
2	+1	-1	0	0	0
3	-1	+1	0	0	0
4	-1	-1	0	0	0
5	0	0	+1	+1	0
6	0	0	+1	-1	0
7	0	0	-1	+1	0
8	0	0	-1	-1	0
9	0	+1	0	0	+1
10	0	+1	0	0	-1
11	0	-1	0	0	+1
12	0	-1	0	0	-1
13	+1	0	0	0	0
14	+1	0	0	0	0
15	-1	0	0	0	0
16	-1	0	0	0	0
17	0	0	0	0	0
18	0	0	0	0	0
19	0	0	0	0	0
20	0	0	0	0	0
21	0	0	0	0	0
22	0	0	0	0	0
23	0	0	0	0	0

	Variable Number				
Trial	1	2	3	4	5
24	0	+1	+1	0	0
25	0	+1	-1	0	0
26	0	-1	-1	0	0
27	0	-1	-1	0	0
28	+1	0	0	+1	0
29	+1	0	0	-1	0
30	-1	0	0	+1	0
31	-1	0	0	-1	0
32	0	+1	0	0	+1
33	0	+1	0	0	-1
34	0	-1	0	0	+1
35	0	-1	0	0	-1
36	+1	0	0	0	+1
37	+1	0	0	0	-1
38	-1	0	0	0	+1
39	-1	0	0	0	-1
40	0	+1	0	+1	0
41	0	+1	0	-1	0
42	0	-1	0	+1	0
43	0	-1	0	-1	0
44	0	0	0	0	0
45	0	0	0	0	0
46	0	0	0	0	0

\> TABLE 3: **REVISED SALT CONCENTRATIONS FOR THE "NOMINAL" SIMULANT RECIPE BASED ON 129" HEEL**

CONSTITUENT	FORMULA	WEIGHT
Sodium Nitrate	$NaNO_3$	286 lbs.
Sodium Nitrite	$NaNO_2$	272 lbs.
Sodium Sulfate	Na_2SO_4	170 lbs.
Sodium Bicarbonate	$NaHCO_3$	*
Potassium Nitrate	KNO_3	17.9 lbs.
Sodium Carbonate	Na_2CO_3	48.4 lbs.
Sodium Hydroxide	NaOH	**10.4 lbs.
Sodium Dichromate, Dihydrate	$Na_2Cr_2O_7.2H_2O$	1590 g
Sodium Chloride	NaCl	1310 g
Sodium Phosphate, Dibasic	Na_2HPO_4	950 g
Sodium Molybdate, Dihydrate	$Na_2MoO_4.2H_2O$	226 g
Sodium Tetraborate, Decahydrate	$Na_2B_4O_7.10H_2O$	122 g
Citric Acid, Anhydrous	$C_6H_8O_7$	163 g
Oxalic Acid, Anhydrous	$C_2H_2O_4$	129 g
Tartaric Acid, Anhydrous	$C_4H_6O_6$	180 g
Water	H_2O	1668.0 lbs.
	TOTAL WEIGHT	2483.1 lbs.
Weight of Solids		815.1 lbs.
Weight Percent Solids		32.83 percent

* Note that Sodium Bicarbonate does NOT appear as $NaHCO_3$ at elevated pH's.

** The Sodium Hydroxide (NaOH) value is an approximation to arrive at a pH of 12.1. This value may vary

TABLE 4: Lab-scale "Nominal" Recipe

Simulant	96 mL
Cement/Calcium Nitrate Blend	140.5 g +/- 1.0 g
Antifoam Emulsion	0.3 mL
Sodium Silicate	11.0 g +/- 0.5 g

West Valley Demonstration Project

Doc. Number WVNS-TP-028 A

Revision Number 1

Revision Date 07/16/91

Engineering Release #2076
Per ECN #4429

TEST PROCEDURE

PROCEDURE FOR DEVELOPMENT OF PROCESS CONTROL PARAMETERS
FOR CEMENT SOLIDIFICATION OF SLUDGE WASH LIQUIDS

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WV-1816, Rev. 1

RECORD OF REVISION

PROCEDURE

If there are changes to the procedure, the revision number increases by one. These changes are indicated in the left margin of the body by an arrow (>) at the beginning of the paragraph that contains a change.

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RECORD OF REVISION (CONTINUATION SHEET)

Rev. No.	Description of Changes	Revision on Page(s)	Dated

TABLE OF CONTENTS

>

WVNS-TP-028A

PROCEDURE FOR DEVELOPMENT OF PROCESS CONTROL PARAMETERS FOR CEMENT SOLIDIFICATION OF SLUDGE WASH LIQUIDS

Rev. 1

1.0 SCOPE

1.1 This Test Procedure is being written in partial fulfillment of WVNS-TRQ-028 and WVNS-TPL-70-11. The completion of WVNS-TRQ-028 will be fulfilled under WVNS-TP-028B. The objective of this overall testing criteria is to establish windows for full-scale production of the sludge wash cement waste form within which an acceptable product can be made. This is based upon the requirements stated in appendix A, section VI, of the NRC Technical Position on Waste Form, Rev. 1, dated January 1991. These windows include variances in the major chemical components of the simulated sludge wash liquid, the cement recipe enhancers as well as physical parameters. Laboratory specimens, 2-inch square cubes, will be used in evaluate these windows.

1.2 The work will include the formation of a series of 28 solutions representing variations in the liquid waste chemical components and cement recipe enhancer which will produce 28 individual 2-inch by 2-inch cubes.

1.3 These 28 cubes will be used to screen the degree of interactions between 13 individual components and will be based upon the cube's compressive strength via a Plackett-Burman Screening Design test.

1.4 The 13 individual components will include variation in the chemical constituents of sulfate, nitrate:nitrite ratio, organics, aluminum, pH, phosphate, and borate. Also to be varied will be the physical parameters of total solids, mixtime, water:cement ratio, and the cement recipe enhancers of calcium, antifoam, and sodium silicate.

1.5 After an appropriate curing period, per section 5.1, the laboratory specimens will be subjected to compressive strength testing as per section 6.3. This testing will provide data on the influence of variations of the chemical composition of the sludge wash liquid and the recipe enhancers on the compressive strength of the cement waste form.

1.6 The gel time, free liquid volume, pH of the free liquid and penetration resistance will be measured and recorded for each cube as part of ACM-4801.

2.0 DEFINITIONS AND ABBREVIATIONS

2.1 Definitions

2.1.1 Cement-Dry Portland Type I cement in accordance with ASTM Standard C-150-85.

2.1.2 Antifoam-General Electric AF9020 emulsion of 5 percent dimethlysilicone in nanopure water. This is used as a cement recipe enhancer to prevent air entrapment in the cement matrix during high-speed mixing.

2.1.3 Sodium silicate - is used as a recipe enhancer in the gelling of the cement waste form and prevention of excess bleed water.

2.1.4 Calcium nitrate tetra-hydrate - is used as a recipe enhancer in the setting of the cement waste form.

2.1.5 Cube - 2x2x2-inch mold used to make laboratory specimens.

2.2 Abbreviations

ACM - Analytical Chemistry Method
ASTM - American Society for Testing and Materials
NRC - Nuclear Regulatory Commission

3.0 QUALITY ASSURANCE

3.1 Analytical and Process Chemistry (A&PC) will be responsible for the preparation and testing of the laboratory specimens in accordance with this test procedure and the applicable steps in the appropriate Analytical Chemistry Methods (ACM). A&PC shall verbally notify cognizant Quality Engineer and Quality Service Manager 24 hours prior to commencement of work.

3.2 Quality Assurance Responsibilities

3.2.1 Quality Assurance shall verify all chemical used in testing having the correct chemical formula on container as is required for this test procedure.

3.2.2 Quality Assurance shall provide independent verification of all chemical processing, measuring, mixing, and other processes required to produce the first five cubes. Quality Assurance may perform the above activities on remaining 23 cubes.

3.3 All WVNS personnel are responsible for documenting nonconformances on cube recipes and/or cube preparation. Nonconformances shall be documented using Nonconformance Report Form, WV-9202. Any cube rejected shall be reported and rejected cube documented with data from other cubes.

3.4 A&PC shall maintain material control by labeling all containers used in testing. A bond laboratory notebook will be used to record solution contents and testing observation along with attachment A.

4.0 TOOLS, EQUIPMENT, COMPONENTS, AND REFERENCES

4.1 Tools and Equipment

- Ligntnin Lab Mixer, Model No. TS-1515 with high-shear impeller or equivalent
- 2x2x2-inch plastic American Cube Molds
- 100 milliliter (mL) plastic or glass graduated cylinder with 1 mL divisions
- 500 mL polypropylene plastic bottles
- Corning hot plate or equivalent
- 10 mL glass volumetric flask
- 20 mL plastic scintillation vials
- magnetic stirring plate and magnetic stir bar
- stopwatch or timer accurate to 1 second
- top loading balance readable to ± 0.01 grams (g)
- Blue M Oven Model No. C-2630-Q or Despatch Environmental Chamber Model No. 16301
- Gilson Penetrometer Model No. CT-421
- fine sand or emery paper

4.2 Reagents

- Portland Type I cement
- Calcium Nitrate tetra-hydrate, reagent grade
- Aluminum Nitrate, reagent grade
- Citric Acid Monohydrate, reagent grade

- Oxalic Acid Dihydrate, reagent grade
- d-Tartaric Acid, reagent grade
- Sodium Silicate, 38 weight percent in a water base, technical grade
- Antifoam General Electric AF9020*
- Aluminum Nitrate • 9 H_2O, reagent grade
- Sodium Phosphate Mono hydrate, reagent grade
- Sodium Tetraborate Decahydrate, reagent grade
- Sodium Nitrate, reagent grade
- Sodium Nitrate, reagent grade
- Sodium Carbonate, reagent grade
- Potassium Nitrate, reagent grade
- Sodium Hydroxide, reagent grade
- Sodium Chromate tetra-hydrate, reagent grade
- Sodium Chloride, reagent grade
- Sodium Molybdate Dihydrate, reagent grade
- nanopure or ASTM Type I water

* supplied by IRTS operations

4.3 References

- NRC Technical Position on Waste Form (Revision 1), January 1991
- ASTM C-150-85 "Specifications for Portland Cement"
- ASTM C-109-86 "Compressive Strength of Hydraulic Cement and Mortars (Using 2-in or 50-mm Cube Specimens)"
- WVNS-TPL-70-11 "Test Plan of the Waste Form Qualification Program for Cement Solidification of Sludge Wash Liquid"
- WVNS-TRQ-028 "Test Request for Development of the Process Control Parameters for Cement Solidification of Sludge Wash Liquids"

- ACM-4701 "Destructive Test of 2-inch Cement Cubes"
- ACM-4801 "Cement Test Cube Preparation Method"
- ACM-2401 "Density"
- ACM-2502 "Total Solids" (Microwave)
- ACM-2601 "pH" (Electrode)

5.0 GENERAL INFORMATION

5.1 The compressive strength tests on cement waste form specimens will be used to evaluate the process control parameters and is considered an acceptable criteria for the overall performance of the product as indicated in appendix A, section VI of the NRC Technical Position on Waste Form, Rev. 1, January 1991. Although cement products nominally achieve 75 percent of their strength in approximately 28 days, it has been decided by convention that a curing period of 7 days for laboratory specimens will allow the specimens to gather sufficient strength in order to be evaluated. This curing process for process control parameter cement specimens requires they be placed in an oven or environmental chamber and sealed individually or in a group in plastic bags for 90 $\pm$ 8 hours at 79 $\pm$ 2°C and then a penetrometer test is performed on each specimen to see if the cement has set and must be greater than 700 psi. During the remaining time period, for a total of 7 days $\pm$ 8 hours, the specimens will be cure at 20° $\pm$ 5°C. At this point the specimen will be testing for compressive strength by the applicable steps of ACM-4701.

The results from this testing will provide a basis for the affects of variances which could be experienced in the full-scale process.

6.0 PROCEDURE

- Oven or environmental chamber should be set at proper temperature as defined in section 5.1. Temperature sensing and recording instrumentation shall be calibrated according to ACP 7.1, Rev. 2.

- Balances shall be calibrated according to ACP 7.1.

- Safety procedures should be reviewed in ACP 7.2.

6.1 Prepare 4 liter of a base solution from the recipe presented in table 1. This will be a base solution for the preparation of four 1-liter stock solutions.

6.2 The first stock solution will contain high sulfate and high nitrate:nitrite ratio. Add 208.8 g sodium sulfate, 420.2 g sodium nitrate, and 163.1 g sodium nitrite to 1000 mL of a base solution. The amount of sodium sulfate, sodium nitrate, and sodium nitrite will be added to the stock solution slowly; one component at a time while mixing on a stir plate. The individual component shall be allowed to go into solution before the next component is added and low heating may be applied to accelerate the dissolution process. After this stock is made it will be used to produce cubes 2, 7, 8, 9, 19, 23, and 26 as presented in table 2. T additional component variations for each cube will be added on an individual basis. The variation amounts are presented in table 3. and the variable combination sequence for each cube is presented in table 2.

6.3 The addition of the chemical components of organics, aluminum, phosphate, and boron will be added to each cube solution based upon 100 mL being generated. These chemicals will be added one at a time while mixing on a stir plate, and each will be allowed to go into solution before the next one is added. At this point, the pH of each cube solution will be measured and adjusted according to ACM-2601 with 10N sodium hydroxide and the amount recorded on attachment A. The total solid content for each solution will be measured according to ACM-2502. At this point, adjustments to the total solid content can be made if necessary by the addition of demineralized water to the solution or evaporation of water from the solution by heating. The final density measurement will be performed according to ACM-2401, the total solids measurement according to ACM-2502 and recorded on attachment A.

6.4 Once the cube solution has been generated; it should be labeled with the cube number. All the cube solutions in each stock set will be prepared and then those solutions wil' be made into cement cubes. The water to cement ratio will be calculated based on the equation presented in section 6.26. The proper amount of simulant will be added to the appropriate amount of cement blend, sodium silicate, and antifoam based upon that cube's variable combination presented in table 2 and the amounted presented in table 3. The cube will be made according to the procedure started with section 6.8 and the gel time, free volume liquid, pH of liquid, penetration resistance, and compressive strength will be recorded on WV-2301 from ACM-4801.

6.5 The second stock solution will contain low sulfate and low ni. ate:nitrite ratio. Add 51.0 g sodium sulfate, 74.4 g sodium nitrate, and 163.1 g sodium nitrite to 1 liter of the base solution. Allow the chemicals to go into the solution as stated in section 6.2. This stock will be used to make cubes 4, 5, 6, 11, 13, 16, and 28 as presented in table 2. The additional component variations for each cube will be added on a individual basis. The variation amounts are presented in table 3 and the variable combination sequence for each cube is presented in table 2. The solutions will be made according the sections 6.2 through 6.3 and the simulate waste cement prepared according to section 6.4.

6.6 The third stock solution will contain low sulfate and high nitrate:nitrite ratio. Add 51.0 g sodium sulfate, 420.2 g sodium nitrate, and 163.1 g sodium nitrite to 1 liter of the base solution. Allow the chemicals to go into solution as stated in section 6.2.2. This stock will be used to make cubes 3, 10, 15, 18, 20, 24, and 27 as presented in table 2. The additional component variations for each cube will be added on an individual basis. The variation amounts are presented in table 3 and the variable combination sequence for each cube is presented in table 2. The solutions will be made according to sections 6.2 through 6.3 and simulate waste cement prepared according to section 6.4.

6.7 The fourth stock solution will contain high sulfate and low nitrate:nitrite ratio. Add 203.8 g sodium sulfate, 74.4 g sodium nitrate, and 163.1 g sodium nitrite to 1 liter of the base solution. Allow the chemicals to go into solution as stated in section 6.2.2. This stock will be used to make cubes 1, 12, 14, 17, 21, 22, and 25 as presented in table 2. The additional component variations for each cube will be added on an individual basis. The variation amounts are presented in table 3 and the variable combination sequence for each cube is presented in table 2. The solutions will be made according to sections 6.2 through 6.3 and simulant waste cement prepared according to section 6.4.

6.8 Make a 5 percent antifoam solution. Weight 5.00 $\pm$ 0.05 g of well mixed AF9020 in a 100 mL volumetric flask and dilute to the manufacturer's mark with nanopure water. Mix well and transfer to a beaker with a magnetic stir bar and stir continuously on a stir plate.

6.9 Prepare 2000 g 2.85 percent calcium nitrate tetra-hydrate/cement mixture by added in 57.0 g calcium nitrate tetra-hydrate to 1943 g Portland Type I cement in a 5000 mL beaker and mix the dry ingredient thoroughly. Also prepare 2000 g 11.4 percent calcium nitrate tetra-hydrate/cement mixture by adding 228 g calcium nitrate tetra-hydrate to 1772 g Portland Type I cement in a 5000 mL beaker and mix the dry ingrediant thoroughly.

6.10 Use a 500 mL plastic bottle to make a mixing vessel by evenly cutting off the tip and producing an open-ended cylinder.

6.11 Similarly cut the top off a 250 mL plastic bottle. This container will be used to add the cement/calcium nitrate mixture to the liquid waste.

6.12 Tare the cutoff 250 mL bottle and add the appropriate amount cement/calcium nitrate blend based upon the cu... sequence variation. Record weight on the appropriate form WV-2301 and attachment A.

6.13 Place the cut empty 500 mL mixing vessel prepared in step 6.3.2 under impeller and set mixer speed to 1000 rpm.

6.14 Calculate the amount of simulant necessary to produce the water to cement ratio desired based on the density and total solids information in section 6.3 and the calculation in section 6.26. Dispense the amount by the use of a graduated cylinder.

6.15 Pour the appropriate amount of simulant into the 500 mL mixing vessel. Rinse the graduated cylinder after each use with nanopure water.

6.16 To the simulant, use an Eppendorff pipet and transfer 0.09 $\pm$ 0.006 mL of the 5 percent antifoam mixture from step 6.3.1 for low antifoam variation and 0.6 $\pm$ 0.003 mL from step 6.3.1 for high antifoam variation work. Record on form WV-2301 and attachment A.

6.17 Tare a 10 mL disposable plastic cup and add to it approximately 5.5 ± 0.5 g sodium silicate for low sodium silicate variation and 22.0 ± 0.5 g sodium silicate for high sodium silicate variation. The exact amount transferred will be found to reweighing the cup after the material is poured into the sludge wash. Record the weight on form WV-2301 and attachment A.

6.18 Support the mixer on a lab stand so that the impeller blade is 1/4 to 1/8 inch from the bottom of the 500 mL plastic bottle. Use a wide-mouth clamp to support the 500 mL plastic bottle without crushing the side. Set a timer for 4 minutes if doing low mixtime variation and 16 minutes for high mixtime variation. Record on attachment A.

6.19 Begin the mixing at 1000 rpm and start the timer. Add the dry cement/calcium nitrate mixture to the waste appropriate for your cube preparation presented in table 2 within the first 30 seconds. After 45 seconds, slowly add the sodium silicate within an additional 45 seconds. Continue to mix for the appropriate time.

6.20 After the transfer of the sodium silicate, reweigh the cup and calculate the amount added by difference, record on form WV-2301 and attachment A. While mixing, mark a cube mold with a permanent marker with the date, sample type, numerical identification sequence number, and then weigh the cube mold, record the weight on form WV-2301.

6.21 After completion of the mix, stop the mixer and transfer the contents to a plastic 2-inch cube mold. Fill to the top and transfer the remaining to a 20 mL plastic scintillation vial and seal. After weighing the cube, tare the scale to zero and reweigh the cube with the cement in it. Record the weight on form WV-2301. Determine the wet density of the material by the formula below.

$$\text{Wet Density} = \frac{\text{Total weight of cube (g) - tare weight (g)}}{131 \text{ mL}}$$

Record on form WV-2301. After completing this step, place the cube in a zip-lock plastic bag.

6.22 Clean the impeller with water immediately after pouring.

6.23 Visually check for gelation of the cement in the 20 mL scintillation vial. Check every 5 minutes and do not disturb between these time intervals. Record the time it takes the cement to gel. Gelation is a subjective determination, however gelled cement is indicated when the 20 mL scintillation vial can be tipped slowly to a 90 degree position, parallel to the horizon. The cement should not deform, flow, and will retain a line of form perpendicular to the horizon. Bleedwater may be present; do not interpret as a sign of uncompleted gelation.

6.24 Transfer the cube to a drying oven with the temperature set at 79 ± 2 celsius within 2 hours of preparation and allow to cure in the oven for 90 ± 8 hours. Record on form WV-2301 time, date the cube was made and the time it was placed in the oven and also the start temperature.

6.25 After 24 hours, determine in milliliters the bleedwater in the scintillation vial and also determine the pH by indicator paper; record it on form WV-2301.

6.26 Calculate the water to cement ratio by weight using formula below.

$$R = \frac{(A)\ (B)\ (1-C)}{(D)\ (1-E)}$$

R = Cement to water ratio

A = Volume in milliliters of sample

B = Density value in grams/milliliters of sample

C = Total Solids value in decimal form

D = Weight of cement used in grams

E = Percent calcium nitrate in the cement blend in decimal form

6.27 After 90 hours ± 8 hours, take the cube out of the oven and do the penetration resistance analysis (see section 6.3.22) and record the time, date, and temperature of the cube removal and also the penetration resistance on form WV-2301.

6.28 <u>CAUTION</u>: **DO NOT REMOVE THE CUBE FROM THE MOLD FOR THE PENETRATION TEST AND ONLY WHEN READY TO CRUSH.**

6.29 Using the concrete penetrometer model CT-421; perform the penetration resistance test by removing the cube from the bag and placing the penetrometer plunger in the center of the exposed side of the cube. Make sure the red indicator ring has been set back to the zero mark on the penetrometer. With a steady vertical force push the penetrometer against the cube until the red indicator ring is all the way down the scale when the penetrometer shaft will not penetrate the cement any further.

6.30 On the handle of the penetrometer, read the value on the red indicator ring and record the number on form WV-2301. If the red indicator ring is all the way to the end of the scale, a value of >700 psi shall be recorded.

6.31 When the sample cube is cured for a total of 7 days ± 8 hours, determine the dry density by the formula below.

$$\text{Dry Density} = \frac{\text{Total weight of dry cube (g) - tare weight (g)}}{131 \text{ mL}}$$

Record on form WV-2301.

6.32 Crush the cube according to ACM-4701.

7.0 DATA ACQUISITION

7.1 Two-inch cube preparation and compressive strength information will be recorded on form WV-2301, Rev. 1.

7.2 The cube sequence variations presented in table 2 will be recorded on attachment A.

7.3 Simulant preparation will be performed in accordance with ACP 7.1.

7.4 A brief test summary and records transfer to the MRC, documenting results of the testing shall be issued by the cognizant A&PC scientist per EP-11-003.

TABLE 1: BASE SOLUTION

Constituent	Formula	Grams/Liter
Potassium Nitrate	KNO_3	10.73
Sodium Carbonate	Na_2CO_3	29.03
Sodium Chromate, Tetra-hydrate	$Na_2CrO_4 \cdot 4H_2O$	2.610
Sodium Chloride	NaCl	1.730
Sodium Tetraborate, Decahydrate	$Na_2B_4O^7 \cdot 10H_2O$	0.161
Water	H_2O	1000.00 grams

TABLE 2: TWENTY-EIGHT-RUN PLACKETT-BURMAN SCREENING DESIGN

Note: Before running tests, the order shall be randomized

	Variable Number												
Trial	1	2	3	4	5	6	7	8	9	10	11	12	13
1	+	-	+	+	+	+	-	-	-	-	+	-	-
2	+	+	-	+	+	+	-	-	-	-	-	+	+
3	-	+	+	+	+	+	-	-	-	+	-	-	-
4	-	-	-	+	-	+	+	+	+	-	-	+	-
5	-	-	-	+	+	-	+	+	+	+	-	-	-
6	-	-	-	-	+	+	+	+	+	-	+	-	+
7	+	+	+	-	-	-	+	-	+	-	-	+	-
8	+	+	+	-	-	-	+	+	-	+	-	-	+
9	+	+	+	-	-	-	-	+	+	-	+	-	-
10	-	+	-	-	-	+	-	-	+	+	+	-	+
11	-	-	+	+	-	-	+	-	-	-	+	+	+
12	+	-	-	-	+	-	-	+	-	+	-	+	-
13	-	-	+	-	-	-	-	-	+	+	-	+	+
14	+	-	-	-	-	+	+	-	-	+	+	-	-
15	-	+	-	+	-	-	-	+	-	-	+	+	+
16	-	-	+	-	-	+	-	+	-	+	-	+	+
17	+	-	-	+	-	-	-	-	+	-	+	-	+
18	-	+	-	-	+	-	+	-	-	-	+	+	-
19	+	+	-	+	-	+	+	-	+	+	-	+	+
20	-	+	+	+	+	-	+	+	-	+	+	-	+
21	+	-	+	-	+	+	-	+	+	-	+	+	+
22	+	-	+	+	+	-	+	-	+	-	-	-	+
23	+	+	-	-	+	+	+	+	-	-	-	-	+
24	-	+	+	+	-	+	-	+	+	-	-	-	+
25	+	-	+	+	-	+	+	+	-	+	+	+	-
26	+	+	-	+	+	-	-	+	+	+	+	+	-
27	-	+	+	-	+	+	+	-	+	+	+	+	-
28	-	-	-	-	-	-	-	-	-	-	-	-	-

TABLE 3: VARIABLE CUBE PARAMETERS

Factors	High (+)	Low (-)	Nominal
Chemical Variable Components per 100 mL			
Phosphate (g PO_4/g Cl^-) (Sodium Phosphate, Dibasic)	1.09 g	0.0015 g	0.08 g
Boron (g B/g Cl^-) (Sodium Tetraborate, Decahydrate)	0.134 g	0.0009 g	0.0018 g
Aluminum (g Al/g Cl^-) (Aluminum Nitrate•$9H_2O$)	4.05 g	0.00 g	0.00 g
Organics			
Citric Acid, Monohydrate	0.096 g	0.012 g	0.024 g
Oxalic Acid, Dihydrate	0.095 g	0.012 g	0.024 g
D-Tartaric Acid	0.095 g	0.012 g	0.024 g
pH (10N Sodium Hydroxide)	13.0	11.0	12.0
Physical Variable Components			
Total Solids (%)	37	25	33
Water to Cement Ratio	0.8	0.3	0.61
Mixtime (mins)	16.0	4.0	8.0
Cement Recipe Enhancers Components			
Percent Calcium Nitrate	11.4	2.85	5.7
Antifoam (mL)	0.6	0.09	0.3
Sodium Silicate (g)	22.0	5.5	11.0

ATTACHMENT A

MULTI-VARIENT CUBE WORKSHEET

Date: ____________________ Laboratory ID: ____________________

Cube No.: ________ ________ Stock Solution: ____________________

Component	Variance (+/-)	Amount
Chemical Component Variables		
1. Phosphate (Sodium Phosphate, Monobasic)	( )	________ g
2. Boron (Sodium Tetraborate, Decahydrate)	( )	________ g
3. Aluminum (Aluminum Nitrate ·9 H_2O)	( )	________ g
4. Citric Acid, Monohydrate	( )	________ g
5. Oxalic Acid, Dihydrate	( )	________ g
6. D-Tartaric Acid	( )	________ g
7. pH	( )	________ S.U.
Amount of 10 N Sodium Hydroxide Added		________ mL
Physical Component Variables		
8. Total Solids	( )	________ %
9. Water to Cement ratio	( )	________
10. Mixtime	( )	________ mins
Cement Recipe Enhancers		
11. Calcium Nitrate	( )	________ %
12. 5 Percent Antifoam Solution	( )	________ mL
13. Sodium Silicate	( )	________ g

Analyst: ______________________________ Date: ______________

Approved: ______________________________ Date: ______________

West Valley Demonstration Project

Doc. Number WVNS-TP-028B

Revision Number 0

Revision Date 09/20/91

Engineering Release #2191

TEST PROCEDURE

WATER TO CEMENT RATIO VARIANCE IN SIMULATED SLUDGE WASH

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RLA0510:3RM

RECORD OF REVISION

PROCEDURE

If there are changes to the procedure, the revision number increases by one. These changes are indicated in the left margin of the body by an arrow (>) at the beginning of the paragraph that contains a change.

Example:

> The arrow in the margin indicates a change.

Rev. No.	Description of Changes	Revision On Page(s)	Dated
0	Original Issue	All	09/20/91

RECORD OF REVISION (CONTINUATION SHEE.

Rev. No.	Description of Changes	Revision on Page(s)	Dated

WATER TO CEMENT RATIO VARIANCE IN SIMULATED SLUDGE WASH

REV. 0

1.0 SCOPE

1.1 This test procedure is being written to complete the request initiated under WVNS-TRQ-02[illegible] and WVNS-TPL-70-011. The objective of this overall testing series is to better define the effects of water to cement ratio on the simulated sludge wash cement's gel time, bleed water, penetration resistance and compressive strength

According to results obtained from WVNS-TP-028A and the Plackett-Burman screening matrix used in this test procedure the only observed effect on the cement waste form was determined to be water to cement ratio variance.

1.2 The work will include 18 2-inch square cubes with water to cement ratios from 0.45 to 0.80 at 0.05 increments however at 0.65, 4 cubes will be made at this increment. After an appropriate curing period, per section 5.0, the 2-inch square cubes will be subjected to compressive strength testing per section 6.2.1.

1.3 The compressive strength, bleedwater, pH of the bleed water, and penetration resistance will be measured and recorded for each cube as part of ACM-4801.

2.0 DEFINITIONS AND ABBREVIATIONS

2.1 Definitions

2.1.1 Cement - Dry Portland Type I cement in accordance with ASTM Standard C-150-85.

2.1.2 Antifoam - General Electric AF90290 emulsion of 5 percent dimethlysilicone in nanopure water. This is used as a cement recipe enhancer to prevent air entrapment in the cement matrix during high-speed mixing.

2.1.3 Sodium Silicate - is used as a recipe enhancer in the gelling of the cement waste form and prevention of excess bleed water.

2.1.4 Calcium nitrate tetra-hydrate - is used as a recipe enhancer in the setting of the cement waste form.

2.1.5 Cube - 2x2x2 inch mold used to make laboratory specimens.

2.2 Abbreviations

ACM - Analytical Chemistry Method
ASTM - American Society for Testing and Materials

3.0 QUALITY ASSURANCE

3.1 Analytical and Process Chemistry (A&PC) will be responsible for the preparation and testing of the laboratory specimens in accordance with this test procedure and the applicable steps in the appropriate Analytical and Chemistry Methods (ACM). A&PC shall verbally notify the cognizant Quality Engineer and Quality Manager 24 hours prior to commencement of work.

3.2 Quality Assurance will perform surveillance as required.

3.3 A&PC shall maintain control by labeling all containers used in testing. A bound laboratory notebook will be used to record solution contents and testing observation.

4.0 TOOLS, EQUIPMENT, COMPONENTS, AND REFERENCES

4.1 Tools and Equipment

- Ligntnin Lab Mixer, Model No TS-1515 with high-shear impeller or equivalent
- 2x2x2 inch plastic American Cube Molds
- 100 milliliter (mL) plastic or glass graduated cylinder with 1 mL divisions
- 500 mL polypropylene plastic bottles
- Corning hot plate or equivalent
- 100 mL glass volumetric flask
- 20 mL plastic scintillation vials
- magnetic stirring plate with magnetic stir bar
- stopwatch or timer accurate to 1 second
- top loading balance readable to +/- 0.01 grams (g)
- Blue M Oven Model No. C-2630-Q
- Gilson Penetrometer Model No. CT-421
- fine sand or emery paper

4.2 Reagents

- Portland Type I cement
- Calcium Nitrate tetra-hydrate, reagent grade
- Citric Acid Monohydrate, reagent grade
- Oxalic Acid Dihydrate, reagent grade
- d-Tartaric Acid, reagent grade
- Sodium Silicate, 38 weight percent in water base, technical grade
- Antifoam General Electric AF9020*
- Sodium Phosphate Monohydrate, reagent grade
- Sodium tetraborate Decahydrate, reagent grade
- Sodium Nitrate, reagent grade
- Sodium Nitrite, reagent grade
- Sodium Carbonate, reagent grade
- Potassium Nitrate, reagent grade
- Sodium Hydroxide, reagent grade
- Sodium Chromate, tetra-hydrate, reagent grade
- Sodium Chloride, reagent grade
- Sodium Molybdate Dihydrate, reagent grade
- nanopure or ASTM Type I water

* supplied by IRTS operations

4.3 References

- NRC Technical Position on Waste Form (Revision 1), January, 1991
- ASTM C-150-85-"Specification for Portland Cement"
- ASTM C-109-86 "Compressive Strength of Hydraulic Cement and Mortors (Using 2-in or 50-mm Cube Specimens)"
- WVNS-TPL-70-11 "Test Plan of the Waste Form Qualification Program for Cement Solidification of the Sludge Wash liquid"

- WVNS-TRQ-028 "Test Request for Development of the Process Control Parameters for Cement Solidification of Sludge Wash Liquids"
- WVNS-TP-025 "Procedure for Development of the Nominal Recipe for Cement Solidification of Sludge Wash Liquids"
- WVNS-TP-028A "Procedure for Development of Process Control Parameters for Cement Solidification of Sludge Wash Liquids"
- "Cement Waste Form Process Control Parameters Screening Test Results" Letter NO. CJ:91:0078, To P.J. Valenti, from John Mahoney, August 12, 1991.
- ACM-4701 "Destructive Test of 2 inch Cement Cubes"
- ACM-4801 "Cement Test Cube Preparation Method"
- ACM-2401 "Density"
- ACM-2502 "Total Solids" (Microwave)
- ACM-2601 "pH" (Electrode)

5.0 GENERAL INFORMATION

Test Procedure WVNS-TP-028A Revision 1 was used to evaluate the effects of 13 variables in the cement waste form production through the use of the Plackett-Burman Screening test. The one variable that showed any significant effect on the compressive strength of the cement and secondary effects of excessive bleedwater and gel time was water to cement ratio. This effect was clearly shown to have an almost linear correlation between water/cement and compressive strength and was also demonstrated in WVNS-TP-025 in the total solids variance and water to cement ratio. This effect will be more clearly defined in this test procedure by the use of a single variance analysis of water to cement ratio over a smaller defined window with the evaluation of a large set of data points. The water to cement ratio will be evaluated from 0.45 to 0.8 at increments of 0.05 and a total of

18 cubes will be made based on duplicate cubes being produced at each increment level. The cubes will be cured at 79° +/- 2°C for 90 +/- 8 hours and the remaining time period for a total of 7 days of curing will be a ambient temperature. At this point in time the compressive strength value for each cube will be evaluated according to ACM-4701.

6.0 PROCEDURE

6.1 Prerequisite

- Oven shall be set at a proper temperature as defined in section 5.0. Temperature sensing and recording instrumentation shall be calibrated according to ACP 7.1, Rev. 2.

- Balances shall be calibrated according to ACP 7.1

- Safety procedures shall be reviewed in ACP 7.2

6.2 A nominal recipe simulant shall be prepared (see attachment A) and 2 cubes shall be made starting with a water to cement ratio of 0.45 and continuing to 0.80 in increment of 0.05. The first nine cubes should be made according to section 6.3 thru 6.3.25 within an 8-hour period and the cubes shall be placed in the oven within 1 hours of preparation. The last nine cubes should be made according to section 6.3 thru 6.3.25 within a 8-hour period and the cubes placed in the oven within 1 hours of preparation.

6.2.1 After curing, per section 5.0, the cubes will be subjected to compressive strength testing according to ACM-4701 with the exception that in section 10.1.3, two opposite faces shall be ground with fine emery paper to the tolerances stated in section 9.6.2 of ASTM C-109.

6.2.2 All compressive strength results, gel time, penetration resistance and bleedwater will be recorded on WV-2301

6.3 Make a five (5%) percent antifoam solution. Weigh 5.00 +/- 0.05 g of well mixed AF9020 in a 100 mL volumetric flask and dilute to the manufacturer's mark with nanopure water. Mix well and transfer to a beaker with a magnetic stir bar and stir continuously on a stir plate.

6.3.1 Prepare 3000 g 5.7 percent calcium nitrate tetrahydrate/cement mixture by adding 171 g calcium nitrate tetrahydrate to 2829.5 g Portland Type I cement in a 5000 mL beaker and mix the dry ingredient thoroughly.

6.3.2 Use a five-hundred (500 mL) plastic bottle to make a mixing vessel by evenly cutting off the tip and producing an open ended cylinder.

6.3.3 Similarly cut the top off a two hundred and fifty (250 mL) plastic bottle. This container will be used to add the cement/calcium nitrate mixture to the liquid waste.

6.3.4 Tare the cutoff two hundred-fifty (250 mL) bottle and add 140.5 +/- 1 cement/calcium nitrate. Record weight on the appropriate Form WV-2301.

6.3.5 Place the cut empty five hundred (500 mL) mixing vessel prepared in step 6.3.1 under impeller and set mixer speed to one thousand rpm.

6.3.6 Measure appropriate amount of 29-33 weight percent simulant based on the water to cement ratio and using equation in section 6.3.18 using a 100 mL graduated cylinder and record this amount on Form WV-2301.

6.3.7 Pour the simulant into the 500 mL mixing vessel prepared according to attachment A. Rinse the graduated cylinder after each use with nanopure water.

6.3.8 To the sludge wash, use an Eppendorff pipet and transfer 0.3 +/- 0.006 mL of the 5 percent antifoam mixture from step 6.3.1. Record the volume on Form WV-2301.

6.3.9 Tare a 10 mL disposable plastic cup and add to it approximately 11.00 +/- 0.5 g sodium silicate. The exact amount transferred will be found by re-weighing the cup after the material is poured into the sludge wash. Record the weight on Form WV-2301

6.3.10 Support the mixer on a lab stand so that the impeller blade is one-quarter to one-eighth inch from the bottom of the 500 mL plastic bottle. Use a wide mouth clamp to support the 500 mL plastic bottle without crushing the side. Set timer for 8 minutes.

6.3.11 Begin the mixing at 1000 rpm and start the timer. Add the dry cement/calcium nitrate mixture to the waste within the first 30 seconds. After 45 seconds, slowly add the sodium silicate within an additional 45 seconds . Continue to mix for a total mix time of 8 minutes.

6.3.12 After the transfer of the sodium silicate re-weigh the cup and calculate the amount added by difference, record the weight on Form WV-2301. While mixing, mark on a cube mold with a permanent marker with the date, sample type, numerical identification sequence number and then weigh the cube mold, record this weight on Form WV-2301.

6.3.13 After completion of the 8-minute mix, stop the mixer and transfer the contents to a plastic 2-inch cube mold. Fill to the top and transfer the remaining to a 20 mL plastic scintillation vial and seal. After weighing the cube, tare the scale to zero and re-weigh the cube with the cement in it. Record the weight on Form WV-2301. Determine the wet density of the material by the formula below.

$$\text{Wet Density} = \frac{\text{Total weight of cube (g)} - \text{Tare weight of cube (g)}}{131 \text{ mLs}}$$

Record the wet density on Form WV-2301. After completing this step, place the cube in a zip lock plastic bag.

6.3.14 Clean the impeller with water immediately after pouring.

6.3.15 Visually check for gelation of the cement in the 20 mL scintillation vial. Check every 5 minutes and do not disturb between these time intervals. Record the time it take the cement to gel. Gelation is a subjective determination, however gelled cement can be determined when the 20 mL scintillation vial can be tipped slowly to a 90 degree position, parallel to the horizon. The cement should not deform, flow, and will retain a line of form perpendicular to the horizon. Bleedwater may be present, do not interpret this as a sign of uncompleted gelation.

6.3.16 Transfer the cube to a drying oven with the temperature set at 79 +/- 2 celsius within 2 hours of preparation and allow to cure in the oven for 90 +/- 8 hours. Record on Form WV-2301 the time, date the cube was made and the time it was placed in the oven and also the start temperature.

6.3.17 After 24 hours, determine in mLs the bleedwater in the scintillation vial and also determine the pH by indicator paper (if bleedwater is present); record both on Form WV-2301.

6.3.18 Calculate the water to cement ratio by weight using formula below.

$$\text{Water to cement} = \frac{(A)(B)(1-C)}{(D)(0.943)}$$

A = Volume in mLs of sample
B = Density value in g/mL of sample
C = Total Solids value in decimal form
D = Weight of cement used in grams

6.3.19 After 90 +/- 8 hours, take the cube out of the oven and do the penetration resistance analysis (see section 6.3.22) and record the time, date and temperature of the cube removal and also the penetration resistance on Form WV-2301.

6.3.20 **CAUTION:** Do not remove the cube from the mold for the penetration test. Remove it only when ready to crush.

6.3.21 Using the concrete penetrometer model CT-421, perform the penetration resistance test by removing the cube from the bag and placing the penetrometer plunger in the center of the exposed side of the cube. Make sure the red indicator ring has been set back to the zero mark on the penetrometer. With a steady vertical force push the penetrometer against the cube until the red indicator ring is all the way down the scale when the penetrometer shaft will not penetrate the cement any further.

6.3.22 On the handle of the penetrometer, read the value on the red indicator ring and record the number on Form WV-2301. If the red indicator ring is all the way to the end of the scale, a value of >700 psi shall be recorded.

6.3.23 When the sample cube is cured for a total of 7 days +/- 8 hours Determine the dry density by the formula below

$$\text{Dry Density} = \frac{\text{Total weight of Dry cube (g) - tare weight (g)}}{\text{131 mLs}}$$

Record on the dry density form WV-2301

6.3.24 Crush the cube according to ACM-4701.

7.0 DATA ACQUISITION

7.1 Two inch cube preparation and compressive strength information will be recorded on Form WV-2301, Rev 1.

7.2 Simulant preparation will be performed in accordance with ACP 8.1 and recorded in Laboratory Notebook

7.3 A test summary report, WVNS-TSR-028, documenting the results of this test procedure will be issued by the cognizant engineer and reviewed by the cognizant A&PC scientist.

ATTACHMENT A

SIMULANT RECIPE BASED ON 128.5-INCH HEEL

Constituent	Formula	g/L
Sodium Nitrate	$NaNO_3$	171.5
Sodium Nitrite	$NaNO_2$	163.1
Sodium Sulfate	Na_2SO_4	101.9
Sodium Nitrate	KNO_3	10.73
Sodium Carbonate	Na_2CO_3	29.02
Sodium Hydroxide	NaOH	6.24*
Sodium Chromate Tetrahydrate	Na_2CrO_4 4 H_2O	2.60
Sodium Phosphate Monobasic	NaH_2PO_4 1 H_2O	1.25
Sodium Chloride	NaCl	1.73
Sodium Molybdate Dihydrate	Na_2MoO_4 2 H_2O	0.300
Sodium Borate Decahydrate	$Na_2B_4O_7$ 10 H_2O	0.161
Citric Acid Monohydrate	$C_6H_2O_4$ 1 H_2O	0.240
Oxalic Acid Dihydrate	$C_2H_2O_4$ 2 H_2O	0.238
D-Tartaric Acid	$C_4H_6O_6$	0.238
Water	H_2O	1000g
Weight of Solids		474.8g
Weight Percent of Solids		32.83%

*The Sodium Hydroxide (NaOH) value is approximate, this chemical should be added last and only in the amount to adjust the pH of the solution to 12 +/-0.2 SU.

WEST VALLEY NUCLEAR SERVICES COMPANY
DOCUMENT RELEASE FORM

Document No.: WVNS-TSR-028

Title: SLUDGE WASH CEMENT WASTE FORM QUAL. DEVELOP. OF PROCESS CONTROL PARAMETERS

Revision: 0

Date: 02/06/92

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WV-1008, Rev. 2
DLS0491.R3

TEST SUMMARY REPORT

Rev. 0

TEST/TEST SERIES Sludge Wash Cement Waste Form Qualification
DESCRIPTION Development of Process Control Parameters
TEST REQUEST NO. WVNS-TRQ-026 TEST PLAN NO. WVNS-TP-026
TEST COMMENCEMENT DATE 7/16/91 TEST COMPLETION DATE 7/31/91
Engineering Release #2271, Date 02/06/92

1.0 OBSERVATIONS/COMMENTS

The purpose of this test procedure was to perform qualification work on cement waste forms simulating the cement waste to be generated following sludge washing. The test procedure was divided into parts A and B. Part A, which has been completed, served as a screening test of variables that could effect gel time, bleed water, and 7-day cured compressive strength of 2" x 2" x 2" cubes prepared in the laboratory. Procedure part B would have tested the variables identified in part A under a closer multi-variant lay-out. Due to the immersion ength failure of the nominal cement recipe, part B of this test series was canceled.

2.0 REFERENCES

1) WVNS-TRQ-028 Revision 1, "Test Request for Development of the Process Control Parameters for Cement Solidification of Sludge Wash Liquids", 7-1-91, J. L. Mahoney

2) WVNS-TP-028A Revision 1, "Procedure for Development of Process Control Parameters for Cement Solidification of Sludge Wash Liquids", 7-16-91, L. E. Michnik

3) Letter FH:91:0104, L. E. Michnik to J. L. Mahoney, "Compressive Strength Results from Multi-Variant Simulated Sludge Wash Cement", dated August 2, 1991

4) Letter FH:91:0105, L. E. Michnik to J. L. Mahoney, "Results from Multi-Variant Simulated Sludge Wash Cement", dated August 5, 1991

5) Letter FH:91:0120, L. E. Michnik to J. L. Mahoney, "Initial Test Summary Report on WVNS-TRQ-028 Rev. 1" dated October 8, 1991

6) Letter CJ:91:0078, J. L. Mahoney to P. J. Valenti, "Cement Waste Forr Process Control Parameters Screening Test Results", dated Octc er 8, 1991

7) United States Nuclear Regulatory Commission "Technical Position on Waste Form" Revision 1, January, 1991.

3.0 CONCLUSIONS/ACCEPTABILITY OF RESULTS/OBJECTIVES MET

The acceptability of the objectives from WVNS-TRQ-028 are presented below.

3.1 Screening Tests of 13 Variables (objective 2.1)

Activity

Perform a Plackett-Burm screening test of 13 possible variables that may affect the cure time, presence of bleed water, penetration resistance, and 7-day cured compressive strength of 2" x 2" x 2" cubes prepared with simulants in the laboratory.

Task Accomplished

This task was completed. Twenty-eight 2" cubes were prepared per TP-028A, yielding compressive strengths, gel times, penetration resistances, and bleed water volumes. A full write-up of the results of the screening test can be found in reference 6 listed under Section 2.

The key statistical conclusion is that only the water-to-cement ratio was found to be important in affecting both the gel time and the cured compressive strength. No variation was seen in penetration resistance for the range of variables tested. Bleed water was present on only 3 cubes which were all at both high water-to-cement ratios and high phosphate levels.

3.2 Multi-Variant Testing of Key Variables (objective 2.2)

Activity

Key variables identified under the screening test will be retested under a Box-Behnken multi-variant test program. The tests will evaluate full interaction of the identified key variables.

Task Accomplished

As noted in Section 1, this portion of the test request will not be performed. Results from other test requests on the nominal cement recipe, have shown a failure in immersion strength.

4.0 ACTIONS OUTSTANDING

No activities remain to be completed as part of this test request series.

APPROVAL(S) ____________________ ADDITIONAL REVIEWERS (YES) NO
J. L. Mahoney

L. E. Michnik   A. J. Howell

Quality Assurance   D. C. Meess

West Valley Demonstration Project

Doc Number WVNS-TRQ-029

Revision Number 1

Revision Date 09-05-91

Engineering Release #2053

ECN #4522

TEST REQUEST

PRODUCTION OF CEMENT PRODUCT FROM ACTUAL SLUDGE WASH LIQUID

PREPARED BY ____ G. A. Smith
Cognizant Engineer

APPROVED BY ____ 3-27-91 D. C. Meess
Cognizant System Design Manager

APPROVED BY ____ 3/27/91 D. L. Shugars
Quality Assurance Manager

APPROVED BY ____ 3/28/91 D. J. Harward
Radiation & Safety Manager

APPROVED BY ____ 3/21/91 J. C. Cwynar
Process Control Engineering

West Valley Nuclear Services Co., Inc.

P.O. Box 191

West Valley, NY 14171-0191

BEL0051:3RM

WV-1816, Rev. 1

RECORD OF REVISION

PROCEDURE

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> The arrow in the margin indicates a change.

Rev. No.	Description of Changes	Revision On Page(s)	Dated
0	Original Issue	All	04-04-91
1	Per ECN 4522	All	09-05-91

RECORD OF REVISION (CONTINUATION SHEET)

Rev. No.	Description of Changes	Revision on Page(s)	Dated

PRODUCTION OF CEMENT PRODUCT FROM ACTUAL SLUDGE WASH LIQUID

1.0 INTRODUCTION

> 1.1 This work is required to approximate the full scale sludge wash process that is being developed at the West Valley Demonstration Project (WVDP), on a lab scale. Confirmatory cubes will be made using actual sludge wash solution produced in lab scale tests to determine accuracy or validity of similar tests to be used in the qualification program, per reference 7.1. This work is within the scope of WVNS-TPL-70-11, section 4.6. All work contained in this document will be completed in the WVNS Analytical & Process Chemistry (A&PC) Lab.

The results of solidification (e.g., gel time, free liquid, cement slurry density) will be compared with results of cube set #1 from WVNS-TRQ-028. Also, a decision will be made by the A & PC lab as to the accuracy of the simulant specified in WVNS-TRQ-026

Composition of all four washes will be compared to that specified in reference 7.2 to assess the validity of simulant to be used in future qualification work.

1.2 All work will be performed with an actual high-level waste tank (8D-2) sludge sample. (Reference 7.3)

> 1.3 Testing shall be conducted in accordance with a test procedure, WVNS-TP-029A, issued by the A & PC Lab.

2.0 OBJECTIVE

> **NOTE:** All weights are approximate. Actual weights should be +0.1 grams of given weights, and be recorded per WVNS-TP-029A.

2.1 The sludge sample (approximately 50 grams) shall be "washed" four times. The washes shall attempt to approximate actual sludge washing conditions. (Reference 7.4)

For the first wash, add:

- The 44.8 grams sludge sample. (Sample contains interstitial liquid)
- 573 grams of 8D-2 Supernatant. Analyze supernatant for constituents given in section 2.4
- 70 grams of lab demin water and 5.8* grams of caustic soda (premixed before being added to mixing vessel)

For the second, third, and fourth wash, add:

- 233 grams of lab demin water and 0.45* grams of caustic soda (premixed before being added to mixing vessel)

2.1.1 Demin water should be analyzed for Na, Mg, Ca, SO_4, and K

2.2 Each wash will be 1 day in length and vessel agitation will approximate actual washing procedure. After agitation, the liquid will be allowed to settle for 24 hours. Vessel temperature will be approximate 70°C for agitation.

2.3 After each of the four washes are complete, the resulting wash liquid shall be decanted off the top of the sludge according to WVNS-TP-029 in the following approximate amounts. (Actual weights of decanted solutions shall be determined in WVNS-TP-029, and recorded for each wash.)

Wash 1: 298 grams of solution
Wash 2: 268 grams of solution
Wash 3: 262 grams of solution
Wash 4: 261 grams of solution

A & PC personnel to note:

1. Speed of solids settling
2. Approximate height of mixture and that of settled solids
3. Approximate height after wash solution removed

2.4 The liquid from all four washes will be analyzed for the following:

NO_2	K	PO_4	Ti
NO_3	Na	SO_4	Ca
BO	pH	CrO_4	
Cl	Al	U	
Tc-99	Cs-137	Sr-90	
Alpha Pu	Gross Alpha	Gross Beta	
Specific Gravity	Total Dissolved Solids (TDS)		
Total Suspended Solids (TSS)			

> 2.5 The wash liquid from washes 2, 3, and 4 will be stored in sealed containers separately at the A&PC lab for future testing. Label "WVNS-TP-029A Wash #_____.

---

* Caustic Soda weights given are approximate. Actual weights will be determined by Titrating and will be incorporated into WVNS-TP-029.

\> 2.6 The decant liquid from wash 1 shall be processed through lab ion exchange columns containing zeolite at a rate of between .8 and 1.1 Column Volumes per Hour (CV/H). The configuration of these columns will be determined and is to be specified in WVNS-TP-029A.

The ability to sample between columns is needed. These samples will be taken at the discretion of the cognizant A&PC scientist per WVNS-TP-029. The samples will be analyzed for Cs-137 and Alpha Plutonium decontamination factor (DF). This information will also be needed to calculate Cs-137 and Pu percent breakthrough.

\> 2.7 Once a preset breakthrough point for Cs-137 is reached, the lead column will be taken off line. All further column changing and preparation will be specified in WVNS-TP-029A.

2.8 Step 2.7 will be repeated as often as necessary as determined by Cs-137 breakthrough, to process total wash #1 volume.

2.9 Once all of the liquid has been processed through the columns, the liquid will be analyzed for all constituents listed in step 2.4.

2.10 The resultant "decontaminated" sludge wash solution will be slowly evaporated to a nominal 33 $^{+0}_{-2}$ weight percent Total Dissolved Solids (TDS). (Per reference 7.4) The evaporation will take place in a glass container with a bottom heating unit. At this point lab personnel should note any unusual occurrences that may occur during boiling, e.g. precipitation, scaling on surfaces, etc.

2.11 The resultant "concentrates" will be analyzed per section 2.4. This work can be done in parallel with steps 2.11 through 2.14.

2.12 A&PC will take 100 ml of the nominal 33 wt percent decontaminated solution and make a cube using the recipe developed in WVNS-TP-025, WVNS-TP-026, and applicable steps of ACM-4801.

\> 2.13 The remaining solution will be stored in sealed containers for possible future analysis. Label "WVNS-TP-029A, Wash #___, Concentrates".

2.14 A&PC will perform destructive tests on the cube per ACM-4701.

2.15 All data will be reviewed and approved by a qualified A & PC scientist or A & PC lab technician.

3.0 SAFETY

3.1 Industrial hygiene practices will be as described in the WVNS Hygiene and Safety Manual, WVDP-011.

3.2 Radiological work will be performed in accordance with the WVDP Radiological Controls Manual, WVDP-010.

3.3 Work in the Analytical & Process Chemistry Lab will be performed in accordance with existing A&PC methods (ACM's).

4.0 EQUIPMENT CONFIGURATION

> 4.1 All lab equipment will be set up as directed in WVNS-TP-029A.

5.0 SAMPLING FREQUENCY

> 5.1 Additional samples will be obtained in the quantities and frequencies specified by the cognizant A&PC scientist and will be specified in WVNS-TP-029A.

6.0 PERSONNEL QUALIFICATION

6.1 Testing will be performed by qualified Analytical & Process Chemistry Technicians using Analytical & Chemistry Methods (ACM's) under the cognizance of an A&PC scientist.

6.2 Surveillance activity will be performed by qualified Quality Assurance personnel.

7.0 REFERENCES

7.1 "Technical Position on Waste Form", Revision 1, dated December 1990.

7.2 "Preliminary Flowsheet-Sludge Wash with Existing 8D-2 Heel", EK:91:0047, J. L. Mahoney, dated 03/07/91.

7.3 Work performed with SOP 8-20, "8D-2 Sludge Sampling". Composited in the A & PC Lab on January 10, 1990.

7.4 "Removal of Plutonium from West Valley High Level Liquid Waste", Bray, Hara, Kazmierczak, dated January 1991.

West Valley Demonstration Project

Doc. Number WVNS-TP-029A

Revision Number 0

Revision Date 04/18/91

Engineering Release #2065

TEST PROCEDURE

PROCEDURE FOR CONFIRMATORY CUBE

PREPARED BY L. E. Michnik — Cognizant Engineer — L.E. Michnik

APPROVED BY J.E. [illegible] for D.C. Meess — Cognizant System Design Manager — D.C. Meess

APPROVED BY Russell J. [illegible] 4/17/91 — Quality Assurance Manager — D.L. Shugars

APPROVED BY D.J. Harward 4/17/91 — Radiation and Safety Manager — D.J. Harward

APPROVED BY J.C. Cwynar 4/17/91 — Process Control Engineering — J.C. Cwynar

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RECORD OF REVISION

PROCEDURE

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Example:

> The arrow in the margin indicates a change.

Rev. No.	Description of Changes	Revision On Page(s)	Dated
0	Original Issue	All	04/18/91

RECORD OF REVISION (CONTINUATION SHEET)

Rev. No.	Description of Changes	Revision On Page(s)	Dated

Test Procedure for Confirmatory Cube

1.0 SCOPE

1.1 This procedure is for the preparation of a 2x2x2 inch cement cube made from actual sludge wash liquid generated from WVNS #2: Sludge Wash #1 and Sludge Wash #2 using a nominal thirty-two inch supernatant heel. It provides the procedure required to perform the tests stated in WVNS-TRQ-29 and WVNS-TE-029.1. The cube will also provide information on the reaction of the nominal recipe for cement on actual sludge wash material and determine if any unforeseen constituents are having an adverse effect on the cement product.

1.2 The liquids will be combined and evaporated to approximately one hundred milliliters (mls), which is the minimal volume of liquid required to generate a cube. The total dissolved solids in the concentrated material will have a maximum value of thirty-three weight percent and a minimum value of twenty-nine.

1.3 The data generated from this cube, compressive strength, gel time, bleed water and penetration resistance will be compared to the results obtained using data generated from simulated sludge wash liquid from the nominal thirty-three inch supernatant heel (see Attachment A) produced under WVNS-TRQ-025.

2.0 DEFINITIONS AND ABBREVIATIONS

2.1 Definitions

Cement-Dry Portland Type I cement in accordance with ASTM Standard C-150-85.

Antifoam-General Electric AF9020 emulsion of five percent Dimethlysilicone in nanopure. This is used as a cement recipe enhancer to prevent air entrapment in the cement matrix during high speed mixing.

Sodium Silicate-is used as a recipe enhancer in the gelling of the cement waste form and prevention of excess bleed water.

Calcium Nitrate tetra-hydrate is used as a recipe enhancer in the setting of the cement waste form Cube-2x2x2 inch plastic mold used to make laboratory specimens.

2.2 Abbreviations

ACM-Analytical Chemistry Method

ASTM-American Society for Testing and Materials

3.0 RESPONSIBILITIES

3.1 Analytical and Process Chemistry will be responsible for the preparation and testing of the laboratory specimens in accordance to the applicable steps of the appropriate analytical chemistry methods and WVNS-TP-029A.

3.2 Quality Assurance will provide surveillance to ensure that the requirements of this test procedure and WVNS-TRQ-029 and WVNS-TE-029.1 are satisfied and verify the final concentrate product, witnessing of the cube being made and also the crushing of the cube.

3.3 Radiation & Safety monitors radiation and contamination levels in the laboratory to insure work is conducted in accordance with the Rad Con Manual WVDP-010 Rev 1.

3.4 Process Control Engineering will be responsible for issuing the test summary report,WVNS-TSR-029, in accordance with EP-11-003.

4.0 TOOLS, EQUIPMENT, COMPONENTS AND REFERENCES

4.1 Tools and Equipment

- Lightnin Lab mixer Model No. TS-1515 with high shear impeller or equivalent
- 2x2x2 inch plastic cube molds
- 100 milliliter (ml) plastic or glass graduated cylinder with one ml divisions
- 500 ml polypropylene plastic bottles
- 250 ml borosilicate beaker

- Corning hotplate or equivalent
- 10 ml glass volumetric flask
- 20 ml plastic scintillation vials
- magnetic stirring plate and magnetic stir bar
- stopwatch or timer accurate to one second
- top loading balance readable to ± 0.01 gs (grams)
- Blue M Oven Model No. C-2630-Q or Despatch Environmental Chamber Model No. 16307
- Gilson Penetrometer, Model No. CT-421

4.2 Reagents

- Portland Type I cement
- Calcium Nitrate tetra-hydrate, reagent grade
- Nanopure water or ASTM Type I water
- Sodium Silicate, technical grade*
- Antifoam General Electric AF9020*

* Supplied by IRTS operations

4.3 References

- NRC Technical Position on Waste Form (Revision 1) Dec, 1990
- ACM-4701 "Destructive Test of 2 inch Cement Cubes"
- ACM-2401 "Density" Rev 3
- ACM-2501 "Determination of Total Solids" Rev 2
- "Removal of Plutonium from West Valley High-Level Liquid Waste", Bray, Hara, Kazmierczak, dated January, 1991
- ASTM C 109-86

- WVNS-TPQ-29 "Production of Cement Product for Actual Sludge Wash Liquid"

- WVNS-TE-029.1

- EP-11-003

5.0 GENERAL INFORMATION

5.1 This test will be used to evaluate the nominal cement formulation recipe (see Attachment C) using actual sludge wash and supernatant from tank 8D-2 based upon a thirty-three inch supernatant heel. It will confirm the accuracy of data and observations generated by laboratory simulants (see Attachment D) and determine if any unforseen constituent are having an undesirable effect on the cement product.

6.0 PROCEDURE

6.1 Prerequisite

- Oven or environmental chamber should be set at proper temperature as defined in sec 6.3.17 and monitored by a calibrated thermocouple or thermometer per PRD 8.0 Rev. 1

- Balances shall be calibrated according to ACP 7.1

- Safety procedures should be reviewed in ACP 7.2

6.2.1 The liquids from WVNS 2, Sludge Wash #1 and Sludge Wash #2 ,pre and post concentrated material,(see Attachment B) will be combined in a two-hundred and fifty ml beaker and evaporated slowly, while stirring to reduce splattering. The liquid will be reduced to approximately three-quarters of its initial volume. At this point the total solids will be determined by ACM-2401. If the total solid content is between twenty-nine and thirty-three percent, the evaporation will stop and the solution allowed to cool. If the solid content is lower than twenty-nine percent, evaporation will continue and the liquid tested periodically by ACM-2401 until the specified range of the solids is achieved. At this point the total solid content will be confirmed by ACM-2501.

6.2.2 If the liquid is reduced to the point were solids are falling out of solution, the evaporation should stop and nanopure water should be added in small increments and the solution should be allowed to stir. Water and stirring shall be used to redissolve the solids. A total solid determination should be made and an appropriate amount of water added to achieve the total solids specified.

6.2.3 After the appropriate solid content has been achieved ninety- six mls of the concentrate will be used to make the confirmatory cube as stated in sec 6.3 and the remaining will be used for the analysis stated in WVNS-TRQ-029 sec 2.4.

6.3.1 Make a five (5%) percent antifoam solution. Weigh 5.00 ± 0.05 gs of well mixed AF9020 in a 100 ml volumetric flask and dilute to the manufacturer's mark with nanopure water. Mix well and transfer to a beaker with a magnetic stir bar and stir continuously on a stir plate.

6.3.2 Prepare 200 gs 5.7 percent calcium nitrate tetra-hydrate/cement mixture by adding 11.4 gs calcium nitrate tetra-hydrate to 200 gs Portland Type I cement in a 500 ml beaker and mix the dry ingredient thoroughly.

6.3.3 Use a five-hundred (500 ml) plastic bottle to make a mixing vessel by evenly cutting off the tip and producing an open ended cylinder.

6.3.4 Similarly cut the top off a two hundred and fifty (250 ml) plastic bottle. This container will be used to add the cement/calcium nitrate mixture to the liquid waste.

6.3.5 Tare the cutoff two hundred-fifty (250 ml) bottle and add 140.5 ± 1g cement/calcium nitrate. Record weight on the appropriate Form WV-2301.

6.3.6 Place the cut empty five hundred (500 ml) mixing vessel prepared in step 6.3.2 under impeller and set mixer speed to one thousand rpm.

6.3.7 Measure 96 ± 2 ml of 29-33 Wt% sludge wash from step 6.2.3 using a 100 ml graduated cylinder and record on Form WV-2301.

6.3.8 Pour 96 ml of stimulant into the 500 ml mixing vessel prepared in 10.2. Rinse the graduated cylinder after each use with nanopure water.

6.3.9 To the sludge wash, use an Eppendorff pipet and transfer 0.3 ± 0.006 ml of the 5% antifoam mixture from step 6.3.1. Record on Form WV-2301.

6.3.10 Tare a 10 ml disposable plastic cup and add to it approximately 11.00 ± 0.5 gs sodium silicate. The exact amount transferred will be found by re-weighing the cup after the material is poured into the sludge wash. Record the weight on Form WV-2301

6.3.11 Support the mixer on a lab stand so that the impeller blade is one-quarter to one-eighth inch from the bottom of the 500 ml plastic bottle. Use a wide mouth clamp to support the 500 ml plastic bottle without crushing the side. Set a timer for eight minutes.

6.3.12 Begin the mixing at 1000 rpm and start the timer. Add the dry cement/calcium nitrate mixture to the waste within the first thirty seconds. After forty-five seconds, slowly add the sodium silicate within an additional forty-five seconds. Continue to mix for a total mix time of eight minutes.

6.3.13 After the transfer of the sodium silicate re-weigh the cup and calculate the amount added by difference, record on Form WV-2301. While mixing, mark a cube mold with a permanent marker with the date, sample type, numerical identification sequence number and then weigh the cube mold, record the weight on Form WV-2301.

6.3.14 After completion of the eight minute mix, stop the mixer and transfer the contents to a plastic 2" cube mold. Fill to the top and transfer the remaining to a 20 ml plastic scintillation vial and seal. After weighing the cube tare the scale to zero and reweigh the cube with the cement in it. Record the weight on Form WV-2301. Determine the wet density of the material by the formula below.

$$\text{Wet Density} = \frac{\text{Total weight of cube (g)} - \text{Tare weight of cube (g)}}{131 \text{ mls}}$$

Record on Form WV-2301. After completing this step place the cube in a zip lock plastic bag.

6.3.15 Clean the impeller with water immediately after pouring.

6.3.16 Visually check for gelation of the cement in the 20 ml scintillation vial. Check every five minutes and do not disturb between these time intervals. Record the time it take the cement to gel. Gelation is a subjective determination, however gelled cement is indicated when the 20 ml scintillation vial can be tipped slowly to a 90 degree position, parallel to the horizon. The cement should not deform, flow, and will retain a line of form perpendicular to the horizon. Bleedwater may be present, do not interpret as a sign of uncompleted gelation.

6.3.17 Transfer the cube to a drying oven with the temperature set at 88 ± 2 celsius within two hour of preparation and allow to cure in the oven for 61 ± eight hours. Record on Form WV-2301 time, date the cube was made and the time it was placed in the oven and also the start temperature.

6.3.18 After 24 hours, determine in mls the bleedwater in the scintillation vial and also determine the pH by indicator paper; record it on Form WV-2301.

6.3.19 Calculate the water to cement ratio by weight using formula below.

$$\frac{(A)(B)(1-C)}{(D)(0.943)}$$

A=Volume in mls of sample
B=Density value in gs/ml of sample
C=Total Solids value in decimal form
D=Weight of cement used in gs

6.3.20 After sixty-one hours ± 8 hour take the cube out of the oven and do the penetration resistance analysis (see section 6.3.22) and record the time, date and temperature of the cube removal and also the penetration resistance on Form WV-2301.

6.3.21 **Caution:** Do not remove the cube from the mold for the penetration test and only when ready to crush.

6.3.22 Using the concrete penetrometer model CT-421; perform the penetration resistance test by removing the cube from the bag and placing the penetrometer plunger in the center of the exposed side of the cube. Make sure the red indicator ring has been set back to the zero mark on the penetrometer. With a steady vertical force push the penetrometer against the cube until the red indicator ring is all the way down the scale when the penetrometer shaft will not penetrate the cement any further.

6.3.23 On the handle of the penetrometer, read the value on the red indicator ring and record the number on Form WV-2301. If the red indicator ring is all the way to the end of the scale, a value of >700 psi shall be recorded.

6.3.24 When the sample cube is cured for a total of 7 days ± 8 hours Determine the dry density by the formula below:

$$\text{Dry Density} = \frac{\text{Total weight of dry cube (g)} - \text{tare weight of cube (g)}}{131 \text{ mls}}$$

Record on form WV-2301

6.3.25 Crush the cube according to ACM-4701 using templates Model No. ACM-140

7.0 DATA ACQUISITION

7.1 Two-inch cube preparation and Compressive strength information will be recorded on Form WV-2301, Rev 1.

7.2 Total solid content will be recorded on Form WV-2306

8.0 ATTACHMENTS

A) Composition of Simulant with 33 inch Supernatant Heel

B) Analysis of Sludge Wash liquids

C) Nominal Recipe for Sludge Wash Cement

D) Nominal Cement Recipe Compressive Strength Data

E) Density Worksheet, ACM-2401 Rev 2

F) Total Solids Worksheet, ACM-2501 Rev 2

Attachment A

ION CONCENTRATIONS FOR CEMENT FORMULATION from TABLE 4-8 of Topical Report "CEMENT WASTE FORM QUALIFICATION REPORT - WVDP PUREX DECONTAMINATED SUPERNATANT"

Salt	Formula	g/L	g/L at 33 wt %	LB/20.9 gal **	Mol Wt
Sodium Nitrate	NaNO3	278.344	278.344	48.547	85.010
Sodium Nitrite	NaNO2	143.790	143.790	25.079	69.000
Sodium Sulfate	Na2SO4	35.222	35.222	6.1432	142.060
Sodium Bicarbonate	NaHCO3	19.656	19.656	3.42[illegible]2	84.010
Potassium Nitrate	KNO3	16.753	16.753	2.9220	[illegible]01.100
Sodium Carbonate	Na2CO3	11.661	11.661	2.05[illegible]	[illegible]06.000
Sodium Hydroxide	NaOH	8.100	8.100	1.4127	40.010
Sodium Chromate	Na2CrO4	2.851	2.848	0.4967	161.970
Sodium Chloride	NaCl	2.163	2.163	0.3773	58.450
Sodium Phosphate	Na3PO4	1.754	1.754	0.3060	163.940
Sodium Molybdate	Na2MoO4.2H	0.374	0.374	0.0653	241.950
Sodium Fluoride	NaF		0.000		41.990
Sodium Borate	Na2B4O7	0.665	0.665	0.1159	201.270
H_2O		800.682	1060.000	139.6500	
			0.000		
Citric acid		0.299	0.299	0.0521	192.120
[illegible]ic acid		0.299	0.299	0.0521	126.070
Tartaric acid		0.299	0.299	0.0521	150.090
Total Mole %					
Wt %					
Wt of Solids		522.230	522.227	91.084	
Wt of Solution		1322.912	1582.227	230.734	
Wt % Solids		39.476	33.006	39.476	
			1255.74 ml		

Attachment B

DATA FOR THE LABORATORY SCALE SLUDGE WASTE AT pH 12.5

F. Hara 12/5/90

Sludge shows 29.3 wt % loss on drying at 104°C, 40.7 % loss during wash, and 30.1 wt % insoluble sludge.

Wt of Sludge	196 g	Solid in Sludge	70.8
Density of Sludge (g/ml)			
Raw Super from 8D-2	71.3 g	Vol of Raw Super	60.2
Vol of Wash Water	500 ml	Density of Ray Super	1.184

Wt of Washed Dried Sludge 59.01 g or 30.1% of wet sludge

CHEMICAL ANALYSIS OF LABORATORY SCALE SLUDGE WASHES BEFORE DECONTAMINATION WITH TITANIUM COATED ZEOLITE

Measured Parameters or Laboratory Analysis	First Wash	Second Wash	Third Wash	Fourth Wash	Analysi of washe dried sludge
Lab No (Sa ID)					900330 900331
Wt Super (gram)	468	458	406	484	
Density (g/ml)	1.109	1.032	1.009	1.002	
Vol Super (ml)	422	444	402	483	
Liq Vol in Sludge (ml)	175	175	175	175	
Total Liquid Vol (ml)	597	619	577	658	
pH	11.87	11.58	11.63	11.59	
Nitrite (ug/g soln)	21100	6080	2070	580	
Nitrate (ug/g)	20600	5680	1830	399	
Sulfate (ug/g)	25400	6620	2340	593	
Chloride (ug/g)	978	614	22	14	
Phosphate (ug/g)					
Sodium (ug/g) AA	44880	11510	4190	1710	47
Potassium (ug/g) AA	1900	710	230	(.53)?	
Uranium (ug/g) Fluorimeter	150	36	3.2	1.6	44100
Cr (ug/g) AA Tot	157	23	11	2.6	
Ca (ug/g) AA	12.4	9.24	3.08	0.57	18370
Al (ug/g)	1000	180	100	60	18067
Ba (ug/g)					8900

Attachment B
(cont'd)

CHEMICAL ANALYSIS OF LABORATORY SCALE SLUDGE WASHES BEFORE DECONTAMINATION WITH TITANIUM COATED ZEOLITE

Measured Parameters or Laboratory Analysis	First Wash	Second Wash	Third Wash	Fourth Wash	Analysis of washed dried sludge
Lab No (Sa ID)					
Pu239 (uCi/g)	0.198	0.026	0.00732	0.0012	
Total Pu (uCi/g)	0.292	0.0382	0.0105	0.0016	101
Sr 90 (uCi/g)	0.282	0.0963	0.0.00203	0.00909	57000
Cs 137 (uCi/g)	418	118	41.4	11.9	291
Co 60 (uCi/ml)	ND	ND	<6.5E-3	<2.4E-4	
Tc 99					
Sb 125	<5.7E-1	<1.6E-1	<7.2E-2	<6.0E-3	
Eu 154	<1.8E-1	<4.8E-2	<2.7E-2	<1.2E-3	
[illegible] 155	<7.4E-1	<2.3E-1	<1.3E-1	<2.5E-3	
Gross Alpha					1210
Gross Beta					127000
TDS (Wt %)	10.7	4.19	0.76	<0.1	
TDS from Decon Wash	13.93	5.48	1.13	0.53	
Grams of TDS from WVNS-2	65.19212	25.64629	5.288377	2.480389	
200,000 gal of super.	68.16050	20.27452	5.56	1.79	

Attachment B
(cont'd)

11/6/90 F. Hara
SLUDGE WASH OF WVNS-2 AT 70°C
DATA FOR THE LABORATORY SCALE SLUDGE WASH AT pH 12.5

Wt of Sludge (gram)	196 grams	Solid in Sludge	
Density of Sludge (g/ml)			
Raw Super frm 8D-2 (ml)		Solids in Raw Super	
Vol of Wash Water		Density of Raw Super	

CHEMICAL ANALYSIS OF SLUDGE WASH - AFTER DECONTAMINATION
WITH TITANIUM COATED ZEOLITE (8 wt% TiO2) COLUMNS

Measured Parameters or Laboratory Analysis	First Wash	Second Wash	Third Wash	Fourth Wash
Wt Super (gram)				
Density (g/ml)	1.102	1.032	1.009	1.002
Vol Super (ml)				
Liq Vol in Sludge (ml)				
Total Liquid Vol (ml)				
pH	11.6	11.67	11.9	11.81
Nitrite (ug/g soln)	21300	6600	1900	510
Nitrate (ug/g)	18700	6070	1700	370
Sulfate (ug/g)	21000	6400	1800	[illegible]
Chloride (ug/g)				
Phosphate (ug/g)				
Sodium (ug/g) AA	44300	16400	4200	1700
Potassium (ug/g) AA	49	21	71	28
Uranium (ug/g) Fluorimeter	52	30	17	1.2
Cr (ug/g) AA Tot	81	27	7.7	2.3
Ca (ug/g) AA	3.7	1.2	20	0.7
Al (ug/g)	820	250	120	77
Pu239 (uCi/g)	1.86E-06	1.65E-06	2.38E-06	6.94E-06
Total Pu (uCi/g)	7.80E-06	2.90E-06	3.51E-06	1.06E-05
Sr 90 (uCi/g)	1.93E-05	1.48E-04	1.20E-05	3.24E-04
Cs 137 (uCi/g)	6.31E-02	1.99E-03	5.82E-05	3.77E-03
Co 60 (uCi/ml)	<ND	<1.5E-5	ND	<1.5E-6
Tc 99	1.30E-01	2.94E-02	1.01E-02	2.80E-03

Attachment B
(cont'd)

CHEMICAL ANALYSIS OF SLUDGE WASH - AFTER DECONTAMINATION WITH TITANIUM COATED ZEOLITE (8 wt% TiO_2) COLUMNS

Measured Parameters or Laboratory Analysis	First Wash	Second Wash	Third Wash	Fourth Wash
Sb 125	<1.5E-4	<9.5E-5	1.18E-03	1.70E-03
Eu 154	<5.2E-5	<5.1E-5	<7.4E-6	<7.9E-6
Eu 155	<3.4E-5	<5.7E-5	<1.4E-5	<2.7E-5
Gross Alpha	5.12E-04	3.84E-04	<.00003	<.00003
Gross Beta	1.32E-01	2.84E-02	8.50E-03	7.32E-03
TDS in wt%	13.93	5.48	1.13	0.53
TSS Wt%	0.11	0.05		

Attachment B
(cont'd)

CONCENTRATION OF DECONTAMINATED LAB WASH
EXPERIMENTAL
CHEMICAL ANALYSIS AFTER CONCENTRATION OF THE DECONTAMINATED WASH SOLUTION TO Wt% DETERMINED

Concentrated SW #	SW #1	SW #2	SW #3	SW #4
			(2.92)	(6.46)
Nitrite (ug/g soln)	61800	48200	48500	25600
Nitrate (ug/g)	64600	50600	46400	34000
Sulfate (ug/g)	44700	50400	51100	33800
Chloride (ug/g)				
Phosphate (ug/g)				
Sodium (ug/g) AA	104400	101000	111000	95800
Potassium (ug/g) AA	1600	1500	1600	1450
Uranium (ug/g) Fluorimeter				
Cr (ug/g) AA Tot	262	200	150	111
Ca (ug/g) AA	8.2	9	14	4
Al (ug/g)	2100	1470	<280	<70
[illegible]9 (uCi/g)				
[illegible]. Pu (uCi/g)	1.64E-05	4.08E-05	6.98E-06	2.30E-05
Sr 90	2.76E-06	2.88E-04	5.02E-05	6.04E-05
Cs 137 (uCi/g)	1.22E-01	1.17E-02	1.43E-03	1.78E-01
Co 60	ND	ND	ND	ND
Tc 99	4.79E-01	3.03E-01	2.28E-01	1.16E-01
Sb 125	<3.05E-4	4.70E-03	1.74E-02	9.40E-02
Eu 154	<9.6E-5	<8.8E-5	<1.4E-4	<3.4E-4
Eu 155	<5.1E-4	<1.06E-4	<1.1E-4	<4.4E-4
Gross Alpha				
Gross Beta				
Density	1.297	1.265	1.26 *	1.26 *
TDS	37.5	33.6	33 wt %*	33 wt %*

* Product diluted to remove from distillation apparatus.

Attachment C

To: John Cwynar
Letter#: FH:91:0018
From: Frank Hara and Larry E. Michnik
Subject: Cement Recipe for Sludge Wash Simulant with 33 inch Supernatant heel
Date: January 24, 1990

The recipe for the laboratory scale specimen cube (2x2x2) contain the following amounts of ingredients:

1) 140.0 grams of Portland Type I Cement with
   5.7% Calcium Nitrate 4 Hydrate

2) 11.0 grams Sodium Silicate

3) 0.3 mls of 5.0 grams to 100 mls antifoam (AF-9020)

4) 96 mls of 33.0 weight percent Sludge wash simulant

This recipe will produce a product with a water/cement ratio of 0.61

illiam F. MacKellar
nager A&PCs

Attachment D
Nominal Recipe Simulant

Template Method
Seven Day Curing

Sample ID	Comp Strength(psi)	Date Prepared
SWCF3 NR 5.7/4	1194	1/23/91
SWCF3 NR 5.7/4	1592	1/23/91
SWCF3 NR 5.7/4	1444	[illegible]/06/91
SWCF3 NR 5.7/4	1208	2/20/91
SWCF3 NR 5.7/4	1358	2/20/91
SWCF3 NR 5.7/4	1331	4/01/91
Average	1331	
Std Dev	167	

Attachment E

DENSITY WORKSHEET

SAMPLE NAME ______________________ LOG NAME ______________

SPECIAL INSTRUCTIONS ____

____

Instruments Used:

SAMPLE ID					QC STANDARD
SAMPLE VOL. (A) mL					
FLASK + SAMPLE (B) g.					
FLASK (C) g.					
LABORATORY TEMP. °C					
TEMP. CORRECTION FACTOR (D)					
SAMPLE DENSITY $\frac{(B-C)}{A} \times D$ (g/mL)					

If % TDS Requested:

120.640177 (Sample Density) - 119.09553 = % TDS

Sample has ____________ % TDS

ANALYST ______________________ DATE ____ __________

APPROVED _____________________ DATE ______________

Attachment F

TOTAL SOLIDS WORK SHEET

Page ___ of ___

AMPLE NAME ______________________ LOG NAME ________________

PECIAL INSTRUCTIONS ______________________________________

____

alance (Model and S/N): ___________________________________

ample Drying Method:

ven (yes/no) S/N: ________________ Hot Plate (yes/no) __________

AMPLE ID					
RY DISH (g) = W_o					
+ SAMPLE (g) = W_s					
RIED SAMPLE + DISH g) = W_D					
OTAL SOLIDS (%) $\frac{_D - W_o}{_s - W_o}$					

ANALYST ____________________ DATE ____________

APPROVED ____________________ DATE ____________

ALCULATIONS: Total Solids (%wt) = $\frac{W_D - W_o}{\quad} \times 100$

WVNS-TSR-029

Enngineering Release #2149
Per ECN #4618

TEST SUMMARY REPORT

REV. 1

TEST/TEST SERIES Sludge Wash Cement Waste Form Qualification

DESCRIPTION Cement Product from Actual Sludge Wash Liquid

TEST REQUEST NO. WVNS-TRQ-029 TEST PLAN NO. WVNS-TP-029A

TEST COMMENCEMENT DATE 4/18/91 TEST COMPLETION DATE 8/20/91

1.0 OBSERVATIONS/COMMENTS/REFERENCES:

After release of WVNS-TRQ-029, it was realized that the tests could not be completed as requested. Test Plan WVNS-TP-029A, in fact was written and authorized as a substitute for a portion of the work specified in WVNS-TRQ-029. Specifically, objectives 2.11, 2.12, and 2.14 of the test request were completed per test procedure WVNS-TP-029A.

Test procedure WVNS-TP-029A combined the remaining portions of laboratory-decontaminated sludge wash solutions from previous experiments into one collective sample. The sample was sampled for analyses and then concentrated prior to creation of a cement cube. The combined wash solution was yellow and slightly cloudy with no observable solids collecting at the bottom of the lab vessel. The original laboratory solutions were filtered before being concentrated.

Following completion of the tests, a test exception was written against the original test request (TE-WVNS-TRQ-029-1) cancelling all other portions of the objectives. The work, as originally defined, is scheduled to be completed under different test requests: WVNS-TRQ-032, WVNS-TRQ-033, and WVNS-TRQ-034.

2.0 REFERENCES

1) Letter FH:91:0073, L. E. Michnik and D. J. Fauth to J. C. Cwynar, "32-inch Heel Sludge Wash Confirmatory Cube," dated May 8, 1991.

> 2) Letter FL:91:0089, L. E. Michnik and R. A. Palmer and R. J. Lewandowski, to J. L. Mahoney, "Initial Test Summary of WVNS-TRQ-029A" dated September 9, 1991.

3.0 CONCLUSIONS/ACCEPTABILITY OF RESULTS/OBJECTIVES MET:

The acceptability of the three objectives retained from WNVS-TRQ-029 are presented below.

3.1 Analyze Concentrates (objective 2.11)

Activity

> Analyze the concentrates used in the preparation of a cement cube.

Task Accomplished

> Following concentration and filtration through a 0.45μ filter, the liquid was sampled and analyzed. The results are presented in Table 1. Physical data for the concentrates are a density of 1.23 gm/ml with a weight percent Total Dissolved Solids (TDS) of 29.7. This meets the defined acceptance window of 31 ± 2 weight percent TDS (section 1.2 of WVNS-TP-029A)

Two requested analyses could not be completed. There was an insufficient amount of undissolved solids in the concentrates such that the percent Total Suspended Solids (TSS) could not be measured. This result was expected and confirmed via this measurement. The other analysis not completed was for phosphate. With this matrix, the Ion Chromatograph was not capable of detecting phosphate. A new method would be needed for phosphate measurement. In future tests, total phosphorous (P) will be measured with the ICP-AES and the equivalent phosphate (PO_4^{-3}) calculated.

3.2 Prepare a Reference 2-inch Cement Cube (objective 2.12)

Activity

Use the concentrates to prepare a reference 2-inch cement cube per the standard Analytical Chemistry Method (ACM).

Task Accomplished

The cube was prepared. A cement slurry density of 1.76 gm/ml was measured. A gel time of 35.5 minutes in the A&PC lab matches very well to general guides maintained by L. E. Michnik, A&PC Cognizant Scientist. The results prior to curing are very acceptable for a cement waste form that meets the 10 CFR 61 criteria and general guides for CSS operation per WVNS-PCP-01.

3.3 Perform Tests on the Cement Cube (objective 2.14)

Activity

Check for bleedwater at the end of a 24-hour period following pouring of the cement cube. Perform a penetration test on the cube after a 61-hour cure at elevated temperature; also complete a destructive compressive strength measurement of the cube following a 7-day curing period.

Task Accomplished

No bleedwater was detected for this cement recipe at the 24-hour mark. An initial curing cycle of 61 hours at 88 ± 2°C was completed. Penetration testing following the 61-hour period yielded a value of >700 psi (beyond range of penetrometer) which is typical and very acceptable for laboratory cubes.

Following completion of a seven day curing period (total time), destructive compression testing on the cube was performed. The cube was compressed using templates (not recognized yet in ASTM-C-109). The result (694 psi) exceeds the minimum mean strength (500 psi) specified in the NRC Technical Position on Waste Form, Revision 1.

For comparison three cubes were prepared in the A&PC lab using reagent grade chemicals to simulate the concentrates used in this experiment. The three cubes used a simulant recipe as shown in Table 2. Trace levels of organics in the recipe are about 30 percent higher than the level defined for sludge wash solution with a 129-inch heel.

The results of compressive strength crushing (using templates) for the three cubes were 841, 1079, and 1138 psi. Combined with a t-statistic of 2.92, the range of strengths that should cover 95 percent of a gausian distribution go from 560 psi up to 1478 psi. This implies that the simulant cubes are exhibiting the same compressive strengths as the laboratory concentrates cube.

The conclusion of this work is that the nominal recipe developed for sludge washing is acceptable although the cube was representative of sludge washing with a 32-inch heel. Additional experiments are defined in WVNS-TRQ-032, WVNS-TRQ-033, and WVNS-TRQ-034 to confirm the cement recipe for sludge washing with a 129-inch heel.

4.0 ACTIONS OUTSTANDING:

> No actions remain outstanding for closure of this test series.

APPROVAL(S) J. L. Mahoney   ADDITIONAL REVIEWERS: (YES) NO

G. A. Smith   J. C. Cwynar   L. E. Michnik

D. C. Meess   Quality Assurance

TABLE 1
Analyses of Laboratory-Produced LWTS Concentrates

units are μgm/gm			units are μgm/gm
Al	1210	NO_2^-	52,300
B	58.4	NO_3^-	42,600
Ca	<15	PO_4^{-3}	Not Measured
Cl^-	3100	SO_4^{-2}	41,200
Cr	161	Ti	<4.7
K	882	U	169
Na	94,700		

pH	12.36
Total Dissolved Solids (TDS)	29.7%
density [gm/ml]	1.23
Total Suspended Solids (TSS)	Insufficient Sample

Units are μCi/gm		units are μCi/gm	
alpha Pu	<5.8E-4	CS-137	0.058
gross alpha	<1.4E-3	Sr-90	2.31E-5
gross beta	0.224	Tc-99	0.227

TABLE 2
Composition of Simulated Sludge Wash

	Dry Weight Percent
$NaNO_3$	25.0
$NaNO_2$	30.2
Na_2SO_4	35.8
$NaHCO_3$	2.69
KNO_3	2.29
Na_2CO_3	1.59
NaCl	0.30
Na_3PO_4	0.24
$Na_2MoO_4.2H_2O$	0.051
$Na_2B_4O_7.10H_2O$	0.091
Citric Acid ($.1H_2O$)	0.082
Oxalic Acid ($.2H_2O$)	0.082
Tartaric Acid (anhydr)	0.082
Na_2CrO_4	0.39
NaOH	1.11

West Valley Demonstration Project

Doc. Number WVNS-TRQ-030

Revision Number 0

Revision Date 05/01/91

Engineering Release #2075

TEST REQUEST

FULL-SCALE CONFIRMATION OF THE NOMINAL RECIPE FOR CEMENT SOLIDIFICATION OF SLUDGE WASH LIQUIDS

PREPARED BY [signature] M. N. Baker
Cognizant Engineer

APPROVED BY [signature] D. C. Meess
Cognizant System Design Manager

APPROVED BY [signature] 4/30/91 D. L. Shugars
Quality Assurance

APPROVED BY GM [signature] For DJH 4-30-91 D. J. Harward
Radiation & Safety

APPROVED BY J. C. Cwynar 4/30/91 J. C. Cwynar
Process Control Engineering

West Valley Nuclear Services Co., Inc.

P.O. Box 191

West Valley, NY 14171-0191

DLS0431:3RM

WV-1816, Rev. 1

RECORD OF REVISION

PROCEDURE

If there are changes to the procedure the revision number increases by one. These changes are indicated in the left margin of the body by an arrow (>) at the beginning of the paragraph that contains a change.

Example:

> > The arrow in the margin indicates a change.

Rev. No.	Description of Changes	Revision On Page(s)	Dated
0	Original Issue	All	05/01/91

RECORD OF REVISION (CONTINUATION SHEET)

Rev. No.	Description of Changes	Revision on Page(s)	Dated

TEST REQUEST

WVNS-TRQ-030
REV. 0

FULL-SCALE CONFIRMATION OF THE NOMINAL RECIPE FOR CEMENT SOLIDIFICATION OF SLUDGE WASH LIQUIDS

1.0 INTRODUCTION

1.1 This work is required to demonstrate the stability of the "nominal" waste form recipe developed under Test Request WVNS-TRQ-026. Characteristics which will be tested are required by 10 CFR 61, Code of Federal Regulations, Title 10, "Licensing Requirements for Land Disposal of Radioactive Waste," and the USNRC Branch Technical Position on Waste Form, Revision 1, dated January, 1991.

1.2 Work will be performed using full-scale square drums which were processed using a simulant representing the actual waste liquid, and the "nominal" recipe for cement addition and recipe enhancers. The full-scale drums will be processed under SIP 91-1.

1.3 This work is required by the Branch Technical Position, Appendix A.II.I.

1.4 Testing will be performed in accordance with WVNS-TP-030, to be issued by Analytical and Process Chemistry, and WVNS-TPL-70-011.

1.5 Test results will be documented in a Test Summary Report (WVNS-TRS-030), to be issued by the Cognizant Test Engineer in accordance with EP-11-003

2.0 OBJECTIVES

2.1 After curing for a time determined by WVNS-TP-026, but in no case less than 28 days, approximately five (5) drums will be core-drilled to obtain 3" diameter X 6" long cylindrical samples. A total of twenty-two (22) samples will be obtained.

2.2 Cores will be obtained from various locations in the drums (top, middle, bottom locations) to demonstrate the homogenous nature of the waste form. Locations will be recorded on SOP-70-44, Attachment D.

2.3 Ten (10) of the samples will be evaluated for compressive strength per ASTM Standard C-39 and QIP 27.

2.4 Twelve (12) of the samples will be immersed in either deionized water or synthetic sea water for a minimum of 90 days. After 90 days' immersion, three (3) of the samples will be evaluated for compressive strength per ASTM Standard C-39 and QIP 27. Post-immersion mean compressive strength shall be at least 75 percent of the pre-immersion mean compressive strength as determined by section 2.3 above and at least 500 PSI. If the post-immersion mean compressive strength is less than 75 percent of the pre-immersion mean compressive strength, but not less than 500 PSI, the immersion testing interval shall be increased to a minimum of 180 days. The remaining samples will then be evaluated for compressive strength at intervals of 120, 150, and 180 days of immersion to establish that the compressive strengths level off and do not continue to decline with time.

2.4.1 The immersion liquid, either deionized water or synthetic sea water, will be determined in advance of this test as part of the Leach Testing being conducted in accordance with WVNS-TRQ-026, Section 2.4.

3.0 SAFETY

3.1 Industrial Hygiene practices will be as described in the WVNS Hygiene & Safety Manual, WVDP-011.

3.2 Radiological work will be performed in accordance with the WVNS Radiological Controls Manual, WVDP-010.

3.3 Work in the Analytical & Process Chemistry lab will be performed in accordance with existing A&PC methods (ACM's).

4.0 EQUIPMENT CONFIGURATION

4.1 All equipment will be set up in accordance with WVNS-TP-030 and as directed by the cognizant A&PC scientist or qualified A&PC technician.

4.2 Core-Boring Equipment will be set up in accordance with SOP 70-44.

5.0 SAMPLING FREQUENCY

5.1 Samples will be obtained in the quantities and frequencies specified by section 2.1 of this Test Request.

5.2 Core-drilling will begin after a minimum cure time of 28 days. The actual cure time will be established in accordance with WVNS-TRQ-026, section 2.2.

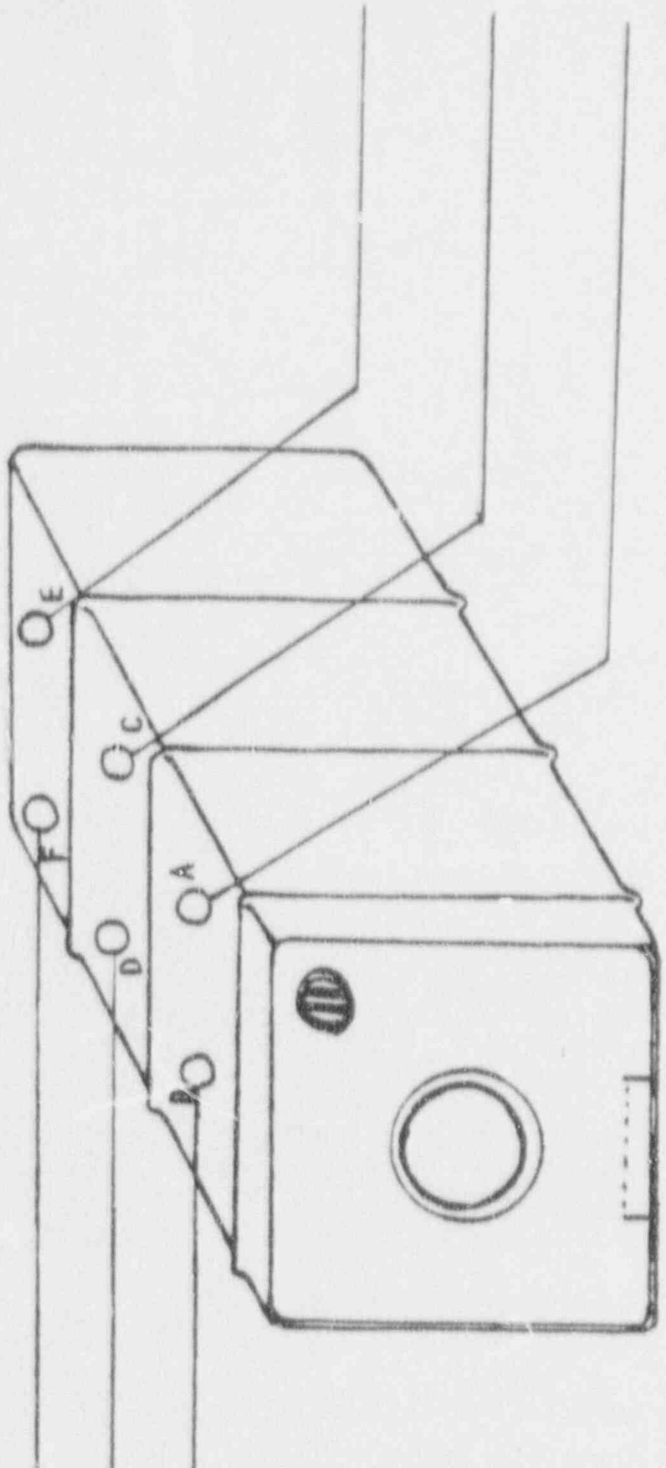
6.0 PERSONNEL QUALIFICATION

6.1 Testing will be performed by qualified Analytical & Process Chemistry Technicians in accordance with WVNS-TP-030 and Analytical Chemistry Methods (ACM's) under the cognizance of an A&PC Scientist.

6.2 Compressive Strength Testing shall be performed by qualified personnel in accordance with QIP-27.

ATTACHMENT D

71 GALLON SQUARE DRUM



DRUM ID NUMBER ____________

Figure 1: Drum Sampling Locations

West Valley Demonstration Project

Doc. Number WVNS-TP-030

Revision Number 0

Revision Date 05/03/91

Engineering Release #2080

TEST PLAN

TEST PLAN FOR FULL-SCALE CONFIRMATION OF NOMINAL RECIPE OF SLUDGE WASH LIQUIDS

PREPARED BY ____ L. E. Michnik
Cognizant Engineer

APPROVED BY ____ D. C. Meess
Cognizant System Design Manager

APPROVED BY ____ D. L. Shugars
Quality Assurance Manager

APPROVED BY ____ D. J. Harward
Radiation and Safety Manager

APPROVED BY ____ J. C. Cwynar
Process Control Engineering

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BEL0079:3RM

WV-1816, Rev. 1

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> The arrow in the margin indicates a change.

Rev. No.	Description of Changes	Revision On Page(s)	Dated
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RECORD OF REVISION (CONTINUATION SHEET)

Rev. No.	Description of Changes	Revision on Page(s)	Dated

TEST PROCEDURE FOR FULL SCALE CONFIRMATION OF NOMINAL RECIPE OF SLUDGE WASH LIQUIDS

WVNS-TP-030
REV. 0

1.0 SCOPE

1.1 This test procedure is being issued in response to WVNS-TRQ-030. The purpose of this test is to correlate the characteristics of full-size products with those of laboratory size specimens in accordance with the requirements of appendix A of the NRC Technical Position on Waste Form, Rev. 1, dated January 1991.

1.2 The full-scale waste form shall be fabricated in the CSS using simulated waste in accordance with SIP 91-01 (20 Drum Run).

1.3 Test specimens (3-inch diameter x 6-inch cylinders) shall be obtained from the full-scale waste form by coring in accordance with SOP 70-44 after a minimum of 28 days cure time.

1.4 Correlation of full-scale characteristics shall be accomplished by performing compressive strength tests on specimens before and after 90 days immersion testing.

1.5 Compressive strength tests shall be conducted in accordance with QIP-027 and ASTM-C-39.

1.6 The pre-immersion compressive strength of the cores will be determined on ten samples. The mean compressive strength of these samples should be at least five-hundred psi.

2.0 DEFINITION AND ABBREVIATIONS

2.1 Definitions

- Demineralized Water- this water must have a conductivity of less than five micromho/cm at twenty-five degrees celsius and a total organic carbon of less than three parts per million.

- Simulated Sea Water-a combination of various inorganic compounds. The formulation is as follows:

23.497	grams	Sodium Chloride
4.981	grams	Magnesium Chloride
3.917	grams	Sodium Sulfate
1.102	grams	Calcium Chloride
0.664	grams	Potassium Chloride
0.192	grams	Sodium Carbonate
0.096	grams	Potassium Bromide
965.551	mL	Demineralized Water

This formulation is from the International Organization for Standardization IOS 1691 1982(E).

2.2 Abbreviations

ACM-Analytical Chemistry Method

ASTM-American Society for Testing and Materials

ANSI/ANS-American Nuclear Standard Institute/American Nuclear Society

QIP-Quality Inspection Procedure

SOP-Standard Operating Procedure

3.0 RESPONSIBILITIES

3.1 Analytical and Process Chemistry will be responsible for the testing of the laboratory specimens in accordance with the ACM-6400 and ACM-6300.

3.2 Quality Assurance provides surveillance to ensure that the requirements of this test procedure are satisfied and will verify those portions of the test where applicable. They also perform the compression testing of cylindrical specimens in accordance with QIP-027 and applicable steps of ASTM C-39.

3.3 Waste Operations will be responsible for core boring the drums in accordance with SOP-70-44.

3.4 IRTS Operations is responsible for making the full-scale drums in accordance with SIP 91-01.

3.5 Radiological work will be performed in accordance with WVNS Radiological Control Manual, WVDP-010.

3.6 Industrial Hygiene practices are described in the WVNS Hygiene and Safety Manual, WVDP-011.

3.7 IRTS Process Control Engineering is responsible for providing technical support of the work outlined in TP-030. They will also issue TSR-030 in accordance with EP-11-003.

4.0 REFERENCES

4.1 NRC Technical Position on Waste Forms (Revision 1), January, 1991.

4.2 ANSI/ANS 16.1 "Measurement of the Leachability of Solidified Low-level Radioactive Wastes by a Short-term Test Procedure".

4.3 ACM-6400 "Immersion Testing of Cement Specimens"

4.4 QIP-27 "Capping and Compressive Strength Testing of Cylindrical Cement Specimens".

4.5 ASTMC-39 "Compressive Strength of Cylindrical Concrete Specimens".

4.6 EP-11-003 "Experimental and Developmental Test Control for High-Level Waste Form Qualification".

4.7 WVNS-TP-026 "Procedure for Qualification of the Nominal Recipe for Cement Solidification of Sludge Wash Liquids"

4.8 ACM-6300 "Leach Index of Cement Specimens".

5.0 GENERAL INFORMATION

5.1 This test will provide information on the correlation of the characteristics of full scale waste form produced from simulated waste with laboratory size specimens.

6.0 PROCEDURE

6.1 Prerequisite

- A determination of the immersion liquid either demineralized water or simulated sea water must be made before immersion testing can be started. The most aggressive leaching liquid or the one that produces the lowest Leaching Index number based upon a twenty-four hour evaluation test, described in ANSI/ANS 16.1 and performed according to ACM-6300, will be used for this test.
- IRTS Operations shall produce the drums in accordance with SIP 91-01.
- The test specimens shall be cured for a time determined by the Cognizant Engineer based on data for TP-026, but in no case less than twenty-eight days.
- Waste Operations will obtain the cores from the drums in accordance with SOP-70-44.
- QA to be notified before start of work.

6.2 Five drums will be cored in accordance with SOP-70-44 and twenty-two samples will be obtained. See attachment A.

6.3 Compressive strength will be determined on ten cores. See attachment A

6.4 The immersion testing on the cores shall be performed in accordance with ACM-6400. See attachment A.

7.0 DATA ACQUISITION

7.1 Compressive strength of the cores will be recorded on data sheets in accordance with QIP-27.

7.2 Core position data will be recorded on data sheets in accordance with SOP 70-44.

7.3 Run data will be recorded per SIP 91-01.

ATTACHMENT A

DRUM TESTING MATRIX

DRUM #	TOP	MIDDLE	BOTTOM
1	C C	1	3 3
5	1	C C	2
10	2	3	C C
15	2 4	C	1
20	C C	4 4	C

C - Compressive strength of samples to be determined.

1 - Sample Set #1. compressive strength to be determined after 90 day immersion testing is complete.

2 - Sample set #2. Compressive strength to be determined, if necessary, after 120 day immersion testing is complete.

3 - Sample Set #3. Compressive strength to be determined, if necessary, after 160 day immersion testing is complete.

4 - Sample Set #4. Compressive strength to be determined, if necessary, after 180 day immersion testing is complete.

WASTE FORM QUALIFICATION PROGRAM FOR CEMENT SOLIDIFICATION OF SLUDGE WASH LIQUID

WEST VALLEY DEMONSTRATION PROJECT

VOL. 2 OF 2

ISSUED 4/16/92

VOLUME II
WASTE FORM QUALIFICATION PROGRAM
FOR CEMENT SOLIDIFICATION
OF SLUDGE WASH LIQUID

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West Valley Demonstration Project

Doc. Number WVNS-PCP-002

Revision Number 0

Revision Date ________

Engineering Release #

PROCESS CONTROL PLAN

PROCESS CONTROL PLAN FOR
CEMENT SOLIDIFICATION OF SLUDGE WASH LIQUID

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SAJ0057:3RM

RECORD OF REVISION

PROCEDURE

If there are changes to the procedure, the revision number increases by one. These changes are indicated in the left margin of the body by an arrow (>) at the beginning of the paragraph that contains a change.

Example:

> > The arrow in the margin indicates a change.

Rev. No.	Description of Changes	Revision On Page(s)	Dated
0	Original Issue	All	

RECORD OF REVISION (CONTINUATION SHEET)

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PROCESS CONTROL PLAN FOR CEMENT SOLIDIFICATION OF SLUDGE WASH LIQUID

Table of Contents

PROCESS CONTROL PLAN FOR CEMENT SOLIDIFICATION OF SLUDGE WASH LIQUID

1.0 SCOPE

This Process Control Plan describes the Cement Solidification Process, its controls, and product quality requirements which will be used during solidification of the sludge wash liquid. The solidification recipe used was developed and demonstrated to comply with the requirements of 10 CFR 61 Section 61.55 and 61.56 for low-level waste stabilization. The recipe was further tested at West Valley to demonstrate process performance and the capability to control the recipe constituents at full scale. This Process Control Plan describes the means of controlling the process to assure that the waste form produced is in conformance with the qualified recipe.

To provide assurance that the waste/cement will perform to its qualified recipe, test cubes will be made, as a minimum for each 5000 gallons of waste to be processed. This will involve one (1) cube for tank 5-D-15A2 (gross capacity 5000 gallons) and two (2) cubes for tank 5-D-15A1 (gross capacity 10,000 gallons).

In order to confirm the uniform nonhazardous nature of the waste form, one (1) sample of the concentrated decontaminated sludge wash will be analyzed for chromium concentration during each Integrated Radwaste Treatment System (IRTS) campaign.

2.0 REFERENCES

Standard Operating Procedures pertinent to this Process Control Plan are listed in attachment A.

3.0 SYSTEM DESCRIPTION

3.1 Process Description

The Cement Solidification System (CSS) includes all piping, valves, instruments, controls, tanks, and equipment required to solidify waste in cement, place it into drums, and remotely move the drums onto a shielded truck for transport to the storage facility. Attachment A (the Run Plan) contains a graphic flow diagram describing the solidification system and its functions, controls and procedures.

The CSS utilizes a high-shear mixer to blend waste, cement and additives into a homogeneous slurry. The impeller located at the bottom of the mixer causes the contents to be drawn to the center of the mixer housing and forces the fluid between the impeller and the casing. This method of mixing ensures thorough and homogeneous blending of all components.

The CSS performs the following functions:

- Waste Solidification - mixing decontaminated sludge wash waste with Portland Type I cement and chemical additives, and packaging the resulting mixture into 269-L square drums.
- Process Control - monitoring and controlling recipe constituent addition, equipment functions and safety interlocks.
- Cement Storage and Transfer - bulk storage of dry Portland Type I cement powder blended with nominally 5.7 $\pm$1.7 (minimum of 4.0, maximum of 7.4) w/o $Ca(NO_3)_2$ and transfer of batch quantities to the mixers.
- Materials Handling - remote handling of empty and filled drums within the facility and loading filled drums onto vehicles for transport to the RTS Drum Cell.

The CSS is composed of the following subsystems:

3.1.1 Waste Storage and Dispensing Subsystem

The Waste Storage and Dispensing Subsystem is the beginning of the treatment process and is composed of the Waste Dispensing Vessel and the Waste Dispensing Pump. The waste liquid is collected and stored here before being mixed with cement; recirculation through the Waste Dispensing Pump maintains homogeneity of the waste while it is stored within the Waste Dispensing Vessel.

Feeds to the Waste Dispensing Vessel are sampled at the final tank feeding the vessel (typically 5-D-15A1 and -15A2 for decontaminated sludge wash solution). Other waste streams will not be added to the Waste Dispensing Vessel during sludge wash processing. The waste feed solids concentration is controlled by the LWTS evaporator at 20 w/o total solids. The allowable range is 19 to 21 w/o. (Product Requirement) The effect of this range is a variance in water-to-cement ratio within the allowable range of 0.64 to 0.68. If necessary, the feed can be diluted to nominally 20 w/o. The method of analysis and tests performed on the samples are discussed in Section 4.0, "Requirements for Sample Verification".

3.1.2 Mixer Flush Subsystem

Whenever the CSS is shutdown for maintenance, or at least at the end of each operating day, the High-Shear Mixers will be flushed to prevent residual cement/waste mixture from hardening inside the mixing vessel.

This process is controlled by the operator at the HS-CSS Panel. When flushing is required, utility water is transferred to each mixer through a spray nozzle with the mixers shut down; the amount transferred is controlled by weight. The mixers are then started on high speed (2000 RPM) creating a highly turbulent transient wave which provides good flushing action. After two or three minutes of agitation at high speed, the flush solutions are dumped into a specially designed decant drum at the fill station. The procedure is repeated with rinse water.

The Flush Drum at the Fill Station is transferred to the Flush Drum Storage Station where the residue is allowed to settle out, the remaining liquid is decanted to an underground storage tank (7-D-13) and will be processed through the existing plant radwaste system. The drum is reused until it is half-full of residue (~102 litres); the drum is then filled with a water/cement mix, and is transported to a storage area. It is expected that each mixer will be flushed prior to system shut down or as required based on mixer build up. Each flush drum holds multiple flushes. If the waste is greater than Class A (see Section 3.3), it will have to be overpacked in a high integrity container prior to disposal.

3.1.3 Chemical Additive Systems (Product Requirement)

Systems are provided to add chemicals to the mixers to accelerate the gelation rate of the waste and control the rate at which the cement sets to minimize buildup of solidified cement in the mixers minimizing the number of flushes required. Calcium nitrate at nominally 5.7 w/o is blended with dry, Portland Type 1 cement by the cement supplier as a gel accelerating component. Testing performed to date indicates that the recipe performance is insensitive to variations in calcium nitrate, and sodium silicate additive over the approved range indicated in the recipe sheets. The acceptance range in calcium nitrate in Portland Type I is 5.7 ±1.7 percent. The blending operation is conducted by a vendor using approved procedures under the WVNS quality assurance program. Samples are analyzed by the analytical laboratory for nitrate concentration to verify acceptable blending by the vendor. Experience has shown that the calcium nitrate does not separate during transport or transfer because it adheres to the cement particles. The dry cement/calcium nitrate blend is stored in the cement silo and is added to the mixers by the cement metering subsystem. Antifoam (GE AF-9020) is added to the mixers with the waste solution to reduce air entrainment in the waste product. Sodium silicate is added to the mixers as the second component of the set enhancer. The amount of antifoam added is shown on the recipe sheets. It is added by injection directly to the mixers from a lab scale positive displacement pump. Only the sodium silicate addition is varied depending on the particular sludge wash waste batch being processed, the remainder of the constituents are held constant. The amount of sodium silicate added to each batch is expected to vary only slightly, if at all, because of the decontaminated sludge wash solutions homogeneity. The amount of sodium silicate to be added is nominally 18 pounds per batch. The homogeneity of the sludge wash being processed is such that valid solidification results can be gained on a sample of the full batch. Full scale recipes for TBD to TBD gallons of waste are contained in Section 3.5.

Homogeneity of the calcium nitrate cement blend is assured through the use of an approved blending procedure submitted by the supplier, periodic quality assurance of the supplier's blending operation and chemical analysis of the blend to assure homogeneity.

3.1.4 Cement Transfer and Storage Subsystem

The Cement Storage and Transfer System provides a bulk storage capacity of 70 m^3 (about 100 tons) for the dry cement/calcium nitrate blend and transfers it to the Cement Metering Subsystem. The blend is delivered from off-site by truck and transferred pneumatically to the Bulk Storage Silo. The transfer air exits the silo through a dust filter at the top. A blower is used to pneumatically transfer the blend to the Acrison day bin in the Cement Metering Subsystem on demand. The transport air is vented back to the Bulk Storage Silo where it vents through a dust filter.

3.1.5 The Cement Metering Subsystem (Product Requirement)

This subsystem uses a gravimetric (loss-in-weight) feeder to accurately dispense the Portland Type 1 dry cement/calcium nitrate blend from the Acrison day bin into the mixers. A bulk dry cement storage silo is located near the CSS to facilitate the filling of the day bin and minimize dust inside the facility.

3.1.6 The High-Shear Mixing Subsystem

Batch control for the High-Shear Mixer is automatic, the operator sets the panel controls for the recipe to be processed and initiates the process. The process parameters are controlled automatically by the HS-CSS programmable logic controller (see Section 3.6). The waste feed, cement/calcium nitrate blend, and additives are metered into the mixer, which runs continuously during operation. The batch is mixed to assure homogeneity and is discharg[illegible] to the waste drum (typically 269L square drums). The process is controlled to assure the recipe is followed and the container is filled to greater than 85 percent capacity.

3.1.7 Drum Feed, Positioning and Transfer Subsystem

A remotely operable conveyor system is installed at CSS to:

- o Move empty drums into the Process Cell,
- o Place drums in position for filling,
- o Read drum dose rates and bar code labels for drum identification,
- o Manipulate filled drums to the smear station for surface contamination measurements and to the overpack station if required,
- o Install and crimp lids on filled drums,
- o Provide for storage of drums prior to load-out from the facility,
- o To transfer filled drums onto the shielded truck for transport to the drum cell, and
- o Periodically test drums for fill, free water and penetration resistance.

3.2 Process Chemistry Formulation for Decontaminated Sludge Wash

Portland Type I cement and waste alone do not produce an acceptable product because of the delay in gelation and ultimately the set time. It is necessary to utilize admixtures of constituents normally present in both the waste stream and the Portland cement to accelerate gelation assuring proper dispersal of waste in the matrix by preventing cement particle settling and setting of the final product in a reasonable time period following production. Early gelation is required to permit timely transport of drums to the storage area.

Prior to transferring waste from LWTS to the Waste Dispensing Vessel, the concentrates collection tank (either 5-D-15A1 or 5-D-15A2) is sampled. Sufficient sample volume is collected for radiochemical analysis and preparation of a verification sample for solidification. Due to its larger operating volume, tank 5D-15A1 is sampled prior to solidification and also at 50 percent ±10 percent level as an in-process check. The second sample will be for presolidification testing only. The purpose of these samples is to assure that the batch of waste to be transferred can be properly solidified using the reference qualified recipe and to provide isotopic analysis for waste classification. The results of the isotopic analysis can be correlated with the waste solution composition. The requirements for sample verification are contained in Section 4.0. The process control systems and logic used to assure that the product is produced in accordance with the qualified formulation is described in Section 3.6, Process Control System.

3.3 Handling Flush Drums and Drums Suspected to be in Noncompliance

As described in Section 3.1, mixers may be periodically flushed to maintain them free of excessive cement buil ρ. The residual flush water will be decanted from the drums leaving behind a relatively dry cement product. The residual cement following decanting will be capped with a cement and water mix specified in a flush recipe to provide a means of solidifying any small amount of free water that may remain on the surface of the decanted cement. Since the cement remaining after decanting consists of residuals from several batches, its qualification and classification are uncertain. These drums will not be processed for immediate disposal, but will be transferred to a storage area where the cement will be allowed to set. The drums will be classified and transferred into a high-integrity container (if necessary) prior to ultimate disposal. Those flush drums which qualify as Class A waste will be stored for later disposal in the Class A disposal facility.

Even though the process is well controlled to produce a product meeting the qualified product characteristics, it may be possible through process upsets to produce material which is outside the qualified region. These containers are referred to as "suspect drums" and could be "out-of-specification" as a result of variations in PRODUCT REQUIREMENTS or PROCESS REQUIREMENTS. PRODUCT REQUIREMENTS will be those necessary to produce an acceptable waste form per 10CFR61. PROCESS REQUIREMENTS will be those necessary for smooth operation fn the Cement Solidification System.

PRODUCT REQUIREMENTS include: Water-to-cement ratio, percent solids in the waste, sulfate percent of total solids, drum percent full, free water in the drum, verification (cube) compressive strength, and addition of recipe admixtures.

PROCESS REQUIREMENTS include: mix time, gel time of presolidification verification (cube) sample and data base corrections.

All "suspect drums" resulting from process upsets will be evaluated on a case-by-case basis, and documented on a Nonconformance Report. Upsets in PRODUCT REQUIREMENTS will be set aside for further evaluation, including compressive strength and leachability testing. A critique will be held to investigate the cause of the upset, and prevent recurrance. Upsets in PROCESS REQUIREMENTS will be set aside until a technical evaluation can be completed to determine product acceptability.

Drums originally considered "suspect" that are found to be acceptable after technical evaluation or testing will be placed in the D.um Cell stack. For upsets in PRODUCT REQUIREMENTS, the Nonconformance Report will be referenced on the drum data base, documenting the upset condition, evaluatior or test results, and corrective actions(s).

Those containers which are unacceptable for disposal will be removed from storage and will be placed in high-integrity containers prior to disposal.

3.4 Drum Fill (Product Requirement)

Drums produced for disposal must be at least 85 percent full of qualified cement product or other suitable inert backfill which meets the 10CFR61 requirements. The drum fill is controlled through the volume of waste, admixtures, and cement prepared for addition to the drum by each mixer and may be verified by load cell weight indication. A representative sample of ...nk 5D-15A1 or 5D-15A2 is analyzed for cesium, strontium, plutonium, and sulfate and total solids. Once this data is known, the data in table I on pages TBD through TBD is used to determine both waste and ce.ent addition criteria. Table usage is based on determinatian o. total solids concentration in the waste combined with reci.e batch size (e.g., 20 gallon batches) to achieve the desired drum fill. Waste and cement (with calcium nitrate) additions are preprogrammed into the HSCSS and acrison control panels such that feed to the mixers is controlled and monitored.

One drum per each process Tank 5D-15A1 or 5D-15A2 is physically inspected for freeboard determination, free liquid presence and per-trometer resistance. The sludge wash solution to be processed i very homogeneous so it is unlikely that modification of the recipe will be required during the processing period for either tank (usually 2-4 days). The drum that is physically inspected is considered to be representative of t.. entire batch of drums from either 5D-15A1 or 5D-15A2.

Tables TBD thru TBD show the calculated range of drum fills produced, acceptable recipe variations, the amount of each constituent to be added, and the water to cement ratio. Percent fill is verified by the Data Acquisition System based on the weight of constituents added to the mixer within the acceptable fill range.

3.5 System Operation

Before beginning any processing of decontaminated waste from the LWTS storage tanks, a successful sample verification must be completed in accordance with the Sample Verification Procedure of Section 5.0. The successful sample solidification parameters are recorded on the Solidification Data Sheet. These parameters are used to verify that the reference recipe is either acceptable as specified or to specify minor changes to the recipe within the qualified region.

Table I - Summary of CSS Waste Stream Formulations

10A	-	[illegible] Gallons/Mixer Batch
10B	-	18.5 Gallons/Mixer Batch
10C	-	19.0 Gallons/Mixer Batch
10D	-	19.5 Gallons/Mixer Batch
10E	-	20.0 Gallons/Mixer Batch
10F	-	20.5 Gallons/Mixer Batch

Notes for Table 10A - 10F

1. Drum volume accounts for plastic liner.
2. Calcium addition based on 5.7 w/o nominal of cement.
3. Sodium silicate addition based on 12.4 w/o of water in sludge wash solution
4. Antifoam emulsion added at 0.57 to 0.76 ml/gallon of sludge wash solution

CSS WASTE STREAM RECIPE

TABLES 10A THRO``H 10F

TABLE 10A
CSS WASTE STREAM RECIPE

WASTE STREAM FORMULATION - 18 GALLONS SUPERNATANT PER MIXER BATCH

SP.GR (SOL'N)
SOLIDS (SOL'N)
GALLONS (SOL'N)
NOM RATIO
CaNO3 (lb)
NaSi (lb)
MIN ANTIFOAM (ml)
MAX ANTIFOAM (ml)
WASTE (SOL'N)

(sec)

MENT(+CaNo3)

ASTE

X WASTE

MIN CEMENT(+CaNo3)

MAX CEMENT(+CaNo3)

MIN RATIO

MAX RATIO(+Na&Ca)

MIN DRUM WT +Na&Ca

MAX DRUM WT +Na&Ca

LB BATCH/MIXER

DRUM % Full

SLURRY DENSITY

TABLE 10B

CSS WASTE STREAM RECIPE

WASTE STREAM FORMULATION 18.5 GALLONS SUPERNATANT PER MIXER BATCH

SP.GR (SOL'N)
SOLIDS (SOL'N)
GALLONS (SOL'N)
NOM RATIO
CaNO3 (lb)
NaSi (lb)
MIN ANTIFOAM (ml)
MAX ANTIFOAM (ml)
LB WASTE (SOL'N)

TIMER (sec)

LB CEMENT(+CaNo3)
MIN WASTE

MAX WASTE

MIN CEMENT(+CaNo3)

MAX CEMENT(+CaNo3)

MIN RATIO

MAX RATIO(+Na&Ca)

MIN DRUM WT+Na&Ca

MAX DRUM WT+Na&Ca

LB BATCH/MIXER

DRUM % FULL

SLURRY DENSITY

TABLE 10C

CSS WASTE STREAM RECIPE

WASTE STREAM FORMULATION - 19.0 GALLONS SUPERNATANT PER MIXER BATCH

SP.GR (SOL'N)
SOLIDS (SOL'N)
GALLONS (SOL'N)
NOM RATIO
CaNO3 (lb)
NaSi (lb)
MIN ANTIFOAM (ml)
MAX ANTIFOAM (ml)

LB WASTE (SOL'N)

TIMER (sec)

LB CEMENT(+CaNo3)

MIN WASTE

MAX WASTE

MIN CEMENT(+CaNo3)

MAX CEMENT(+CaNo3)

MIN RATIO

MAX RATIO(+Na&Ca)

MIN DRUM WT+Na&Ca

MAX DRUM WT+Na&Ca

LB BATCH/MIXER

DRUM % FULL

SLURRY DENSITY

TABLE 10D

CSS WASTE STREAM RECIPE

WASTE STREAM FORMULATION - 19.5 GALLONS PER MIXER BATCH

SP.GR (SOL'N)
SOLIDS (SOL'N)
GALLONS (SOL'N)
NOM RATIO
CaNO3 (lb)
NaSi (lb)
MIN ANTIFOAM (ml)
MAX ANTIFOAM (Ml)

LB WASTE (SOL'N)

TIMER (sec)

LB CEMENT(+CaNo3)
MIN WASTE

MAX WASTE

MIN CEMENT(+CaNo3)

MAX CEMENT(+CaNo3)

MIN RATIO

MAX RATIO(+Na&Ca)

MIN DRUM WT+Na&Ca

MAX DRUM WT+Na&Ca

LB BATCH/MIXER

DRUM % FULL

SLURRY DENSITY

TABLE 10E

CSS WASTE STREAM RECIPE

WASTE STREAM FORMULATION - 20.0 GALLONS SUPERNATANT PER MIXER BATCH

SP.GR (SOL'N)
SOLIDS (SOL'N)
GALLONS (SOL'N)
NOM RATIO
CaN03 (lb)
NaSi (lb)
MIN ANTIFOAM (Ml)
MAX ANTIFOAM (ml)

LB WASTE (SOL'N)

TIMER (sec)

LB CEMENT(+CaNo3)
MIN WASTE

MAX WASTE

MIN CEMENT(+CaNo3)

MAX CEMENT(+CaNo3)

MIN RATIO

MAX RATIO(+Na&Ca)

MIN DRUM WT+Na&Ca

MAX DRUM WT+Na&Ca

LB BATCH/MIXER

DRUM % FULL

SLURRY DENSITY

TABLE 10F

CSS WASTE STREAM RECIPE

WASTE STREAM FORMULATION - 20.5 GALLONS SUPERNATANT PER MIXER BATCH

SP.GR (SOL'N)
SOLIDS (SOL'N)
GALLONS (SOL'N)
NOM RAITO
Ca NO_3 (lb)
Na Si (lb)
MIN ANTIFOAM (Ml)
MAX ANTIFOAM (Ml)

LB WASTE (SOL'N)

TIMER (SEC)

#CEMENT + $CaNO_3$

MIN. WASTE

MAX WASTE

MIN CEMENT & $CaNO_3$

MAX CEMENT & $CaNO_3$

MIN RATIO

MAX RATIO (Na&Ca)

MIN DRUM WT Na&Ca

MAX DRUM WT Na&Ca

BATCH/MIXER

DRUM % FULL

SLURRY DENSITY

Actual full-scale solidification is then conducted in accordance with the Cement Solidification System Run Plan (attachment A).

The sequence of operations is as follows:

- Decontaminated waste is added batchwise to the mixers from the recirculation line of the Waste Dispensing Vessel using the Waste Dispensing Pump.
- The recipe quantity of Antifoam (GE AF-9020) is added to the mixer and the solution mixed at 2,000 rpm for 10 seconds.
- The mixer speed is reduced to 1,000 rpm and cement/calcium nitrate addition is initiated. Metering of the proper amount of dry mixture into the mixer requires between 2 and 4 minutes.
- At the end of the cement feed step, sodium silicate is added in a water based solution. The feed is accomplished with the mixer continuing to run at 1,000 rpm. Mixer speed is monitored. The addition requires less than 30 seconds. A mixing time of 60 seconds is counted from the end of the sodium feed to the opening of the dump valve, which is held open for 40 seconds to discharge the batch into the drum.

3.6 Process Control System

The HS-CSS PLC (Programmable Logic Controller) controls the automatic solidification process. Three independent subprograms exist within the main program, one controlling mixer No. 1, one controlling mixer No. 2, the third controlling the fill nozzle and lid handler/turner with checks for proper drum positioning. This allows single or 2 mixer operation with no reduction in processing rate.

The programs are arranged to permit only the correct operating sequences to occur. Events called for must take place in step or programs are inhibited and addition of any ingredient prevented.

The PLC controls the additions of waste, Antifoam, and sodium silicate and mix time as specified by operator-controlled settings on the control panel.

The DAS (Data Acquisition System) records weights at the direction of the PLC at appropriate program steps. The mixer programs allow repetition of waste and cement feeds in incremental amounts should the weight of the charge transferred be low, as checked by DAS for recipe correlation during the process.

Valve V-2 which discharges liquid waste into the mixers in the automatic mode has been tested and shown to give a 99 percent confidence factor by a regression analysis. The HS-CSS controller provides checks to maintain this accuracy. Among these checks are:

- Before any V-2 operation is allowed, its position indications of "open" and "closed" are checked for nonsimultaneous location,
- To allow V-2 operation, recirculation loop flow must be equal to or greater than 97 percent of expected nominal flow,
- When called upon to open or close, valve response time is monitored and if not proper, the Waste Dispensing Pump is stopped and program is terminated,
- If valve V-14 is not directed to mixer 1 and 2 as called for, the program is inhibited, preventing double batching of one mixer,
- Timing of valve opening is controlled to within 0.1 second. Typical time settings are in range of 12 to 14 seconds.
- The cement mix time sequence is not a variable. It is set and not changed during processing.

The addition of the sodium silicate additive is controlled by an air-operated piston pump; the total volume charged to a mixer is controlled by counts of pump strokes by the PLC. Settings are made by the operators on the control panel based on the recipe requirements. The pumps have been calibrated for a specific discharge per stroke. Out-of-range charging will be alarmed by the DAS, based on mixer weight increase measured by load cells.

A control logic diagram for the HS-CSS control system is shown in Figure 1.

3.7 CSS Data Acquisition System

The CSS Data Acquisition System (DAS) is used to document the processing of each waste drum and of each mixer batch that went into the waste drums. The DAS accepts signals from the mixer load cells, the dry cement metering system, drum dose rate monitor, and bar code reader. The DAS also accepts digital signals from the HSCSS control system to record weight readings for waste and cement at the proper time in the process. Note that back-up data is manually taken as part of the WVNS Standard Operating Procedures.

Insert Figure 1

The Data Acquisition System also is used to insure that each mixer batch is within acceptable limits, as determined by the qualified recipe parameters for min/max waste weight and min/max water to cement ratio. If any one of these parameters is outside the acceptable limits for the mixer batch, the DAS will alarm and alert the operator. At this point, mid stream manual corrections for such conditions as low waste weight or high water-to-cement ratio may be made, while maintaining automatic control, thus assuring that each mixer batch and each waste drum conforms with the qualified recipe. Final drum weight is calculated and recorded by the DAS as the sum of the recipe constituents.

A real time display and printout of all major process steps and alarm conditions is generated using the DAS (an IBM Industrial AT microcomputer system). In addition, the DAS maintains files for all drums made during the course of production. An online display exists to allow instant display of drum/mixer weights, water-to-cement ratios, overpacks and dose rates of any drum monitored by the DAS. A weekly activity file is maintained on disk in order to identify drums made during an operational period. These ASCII formatted drum records may be copied to diskette during nonoperational periods and placed in spreadsheet form for further off-line analysis.

The following is a brief summary of the DAS accuracy in calculating drum weight.

1. The DAS retains the empty* mixer weight reading from the previously weighed batch.

   VARIANCE: Accuracy of mixer load cell (+/- 3 pounds).

2. The DAS first calculates the weight of the added waste. It takes the mixer reading after the waste has been added, and subtracts the empty mixer weight (from step No. 1.).

   VARIANCE: Accuracy of mixer load cell (+/- 3 pounds).

3. The DAS then obtains the weight of the added cement/calcium nitrate from the Acrison System (direct loss-in-weight reading from the cement day bin).

   VARIANCE: Accuracy of Acrison (+/- 2 pounds).

4. The Antifoam agent is then added. The weight for this additive is not computed, as only 10 to 15 millilitres per batch is used.

   VARIANCE: Minor

---

* Empty mixer weight plus any remaining mix.

5. The weight of sodium silicate added is calculated from its density and the volume added as determined by HS-CSS pump stroke data.

VARIANCE: Accuracy of pump stroke times the number of strokes + ½ of a stroke (± 1 pounds)

NOTE: 0.15 litre/stroke and 5 litres required per batch.

Periodic calibration of these pumps is performed as well as trending analysis.

6. After mixing is complete and the batch is dumped from the mixer to a drum, the empty* mixer weight is read.

VARIANCE: Accuracy of mixer load cell (+/- 3 pounds).

7. DAS calculates the batch weight as follows:

BEGINNING EMPTY MIXER WEIGHT (step 1) + TOTAL WASTE WEIGHT (step 2) + TOTAL CEMENT WEIGHT (step 3) + ADMIXTURE (step 5) (-) ENDING EMPTY MIXER WEIGHT (step 6).

8. After both batches have been added to the drum, the DAS calculates the total drum weight as follows:

BATCH #1 WEIGHT + BATCH #2 WEIGHT + TARE DRUM WEIGHT (CONSTANT)

A potential variance of 9 pounds per batch is possible:

Load cell reading two times	2 x 3 = 6
Acrison reading one time	1 x 2 = 2
Admixture one time	1 x 1 = 1

A potential variance of pounds per total drum weight is possible:

Two batch readings per drum	2 x 9 = 18
Variance in empty drum weight	= 5

Based on 20 gallons of waste/batch, average net mix would be about 900 pounds. Using highest drum weight variance (23 pounds), percentage of error is 2.6 percent.

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* Empty mixer weight plus any remaining mix.

NOTES: 1. Mixer being read has no movement - variance of scale is +/- 3 pounds.

2. Effect of mixer 1 (mixing) on reading of mixer 2 (no movement of mixer 2) is +/- 3 pounds.

3. Variance if reading scale while mixer is mixing is +/- 4 pounds.

4. Accuracy and reliability of the dry cement metering system (Acrison feeder) and Waste Metering Valve (V-2) was experimentally determined to be > 99 percent.

5. Empty drum weight has a potential variance of +/- 5 pounds.

4.0 REQUIREMENTS FOR SAMPLE VERIFICATION

The tanks which feed the waste dispensing vessel are sampled using an installed sampling system designed to provide a representative sample of the tanks. The samples are delivered to the Analytical Laboratory where they are analyzed for:

- o Total dissolved solid content,
- o Specific radionuclide analysis for waste classification,
- o pH,
- o Sulfate
- o Density, and
- o Presolidification compressive strength.

These measurements are used to ensure that the waste to be processed at the CSS is compatible with the reference formulation. In addition to these analyses, a sample of the waste is solidified using the reference recipe to assure that a dry, solid final waste form can be produced in the full-scale system. The sample solidification verification requirements and procedures used are discussed in sections 4.0 and 5.0, respectively.

4.1 Laboratory Safety

4.1.1 All safety precautions outlined in Analytical Chemistry Procedure (ACP) 7.2 "Laboratory Safety" must be followed.

4.1.2 While working with radioactive material, ACP 7.4 "Handling Radioactive Materials" must be followed.

4.2 Prerequisites

4.2.1 Representative samples of the decontaminated sludge wash, one sample per nominal 5,000 gallons of waste to be processed is required. (A batch consists of the combined contents of Tank

5D-15A1 and 5D-15A2.) Two samples are obtained from 5D-15A1, one when the tank is full and one at half capacity, and one sample is obtained from 5D-15A2 when it is full, after the tanks have been sufficiently mixed to ensure a homogeneous mixture.

4.2.2 Chemical and radiochemical analyses are performed to include the following:

A. Gross alpha and beta
B. Gamma scan
C. Total solids (TS)
D. Density (ρ)
E. pH
F. Radiochemical analyses for nuclides listed in 10CFR61
G. Sulfate

The analyses will be checked for mutual self-consistency.

4.2.3 Equipment required for test specimen preparations.

A. Sample curing oven, thermostatically controllable in the range of $70^oC \pm 5^oC$ equipped with a calibrated temperature sensing device (Thermocouple).

B. Metler top loading balance sensitive to the nearest 0.01 gram with a loading capacity of at least 1,200 grams.

C. "Lighting Lab Mixer" equipped with variable speed control, watt loading, automatic timer, and high-shear mixing blade.

D. ASTM certified 2-inch cube cement molds.

E. Various containers and glassware as required.

F. Calibrated compressive strength testing instrument.

G. Chemicals

1. Portland Type 1 cement/calcium nitrate mixture obtained from operations.

2. Antifoam agent GE AF 9020.

3. Sodium silicate solution

Silica to soda ratio	3.23 ± .05
Water	62 ± 3%
Na_2O	9.0 ± 0.1%
SiO_2	29.0 ± 0.2%

4.3 Sample Acceptance Criteria

To ensure that an acceptable solidified waste form has been produced, the technician shall verify that all acceptance criteria are met as follows:

4.3.1 Visual inspection of the sample after pouring into the mold to look for any separation of liquid on the surface. If separation occurs, estimate how much and when the liquid separated. Observe the liquid and check for readsorption. If readsorbed, record when. (Product Requirement)

4.3.2 Visual inspection of the 2-inch cube after the cure period shows that a firm dry monolith has formed, and that no degredation (cracking or spalling) has occured.

4.3.3 Compressive strength (ASTM C-109) of the 2-inch cube exceeds TBD psi. (Product Requirement)

4.3.4 Pourability of the mixer is such that retention of product in the mixing container is minimal (<5 percent of constituents).

4.3.5 Gelation is controlled to occur not more than 90 minutes following the pour. (Product Requirement) This range of gel times allows a sufficient amount of gelation prior to transporting the drums of encapsulated waste to the drum cell.

In the event that presolidification cannot be achieved within the qualified recipe range, the process will be stopped. At this point, further qualification testing would be required prior to proceeding.

4.4 Requirements for Sample Verification

4.4.1 Verify that all materials and equipment listed in Section 4.2.3 are ready and available to use in the Radiochemistry Laboratory.

4.4.2 Refer to Section 5.0 as applicable when conducting sample verification. Use the Solidification Data Sheet, Figure 1, for all sample solidifications.

4.4.3 Sample Requirements

A. A sample shall be solidified prior to full-scale solidification of waste.

B. If no additional material has been added to the hold tank (5-D-15A1 or -15A2) after the sample was taken, solidified test specimen is considered representative of tank contents. Note: An additional sample will be removed from 5-D-15A1 at 50 ±10 percent level and used as an in-process check for an additional cube sample verification.

C. Test specimen sample solidification will be performed, thereafter, on each new hold-tank batch of waste to be processed.

D. The technician shall verify that the samples used for the three 2-inch cube specimens are representative of the homogeneous waste samples obtained from the sparged 5-D-15A1 or 5-D-15A2 hold tanks.

5.0 SAMPLE VERIFICATION PROCEDURE

5.1 Operations group will provide the laboratory with 150 mL representative sample of decontaminated sludge wash from either of the feed tanks 5D15A1 or 5D15A2.

5.2 Upon receipt of sample, visually inspect sample for precipitates, insoluble phases or nondissolved suspensions, and record observations on worksheet (figure 3). In the event that undissolved solids are found, the process will be stopped. Mix the sample thoroughly and remove sample for Chemical and Radiochemical analysis using the following Analytical Chemistry Methods(ACM):

NOTE:

THIS METHODOLOGY WILL BE USED UNTIL SUFFICIENT EXPERIENCE AND DATA ARE AVAILABLE TO ESTABLISH WASTE CLASSIFICATION BY KEY ISOTOPE RATIONS. THE DECISION TO UTILIZE RATIONS VERSUS SPECIFIC ISOTOPIC ANALYSIS WILL BE MADE BY THE MANAGER, ANALYTICAL AND PROCESS CHEMISTRY.

5.2.1 Measure gross alpha and beta by ACM-Gross-1201

5.2.2 Measure Sb-125, Cs-137, Am-241 and Co-60 by ACM-Gamma-3101

5.2.3 Measure Tc-99 by ACM-Tc-99-4001

5.2.4 Measure H-3 by ACM-H-3-4301 and EM-13

5.2.5 Measure total Plutonium by ACM-Pu-2701

5.2.6 Measure Sr-90 by ACM-Sr-3001

5.2.7 Measure TS by ACM-TS/TDS-2502

5.2.8 Measure density by ACM-Den-2401

5.2.9 Measure pH by ACM-pH-2601

5.2.10 Measure Sulfate by TBD

5.2.11 Total Carbon by TBD

5.3 Ratio the following radionuclide according to the best data available for rationing (Ratios originally established by Rykken, DOE/NE/44139-14 [DE87005887] "High Level Waste Characterization of West Valley", dated June 2, 1986.) (and TBD)

5.3.1 I-129 ratio to Sb-125

5.3.2 Ni-59 and 63 ratio to Co-60

5.3.3 Cm-242 ratio Am-241

5.3.4 C-14 to total carbon

5.4 Prepare a lab scale sample of sufficient size to make a two-inch cube using the cement/calcium nitrate mixture, antifoam emulsion and sodium silicate used in the plant.

The lab scale recipe must be rigorously scaled down from the plant recipe for producing the waste form.

5.5 The cement is to be prepared per ACM-Cem Prep -4801, preparation of 2-inch square cubes for compressive strength testing.

5.6 Place 2-inch cube mold and sample into cure oven; record oven temperature and time on solidification data sheet.

5.7 Cure sample for a minimum of 24 hours.

5.8 Visually inspect the sample after the cure period in the oven. The sample must be a firm solid cube with no physical degradation and with a compressive strength of greater than TBD psi.

INSERT FIGURE 2- page 1 of 4

Analytical Request - 5D15A1#

INSERT F JRE 2- page 2 of 4

Analytical Request - 5D15A1#

INSERT FIGURE 2- page 3 of 4

Analytical Request - 5D15A1#

INSERT FIGURE 2- page 4 of 4

Analytical Request - 5D15A1#

FIGURE 3

Solidification Data Sheet

Sample Log No. ____________ Time and Date Sample Taken:

Tank Sampled ____________ ____________

Gross alpha ____________ uCi/g TS ______ %

Gross beta ____________ uCi/g Density ______ g/mL

Cs-137 ____________ uCi/g pH ______ SU

SO_4 ______ ug/g

Decontaminated Supernatant Volume ____________ mL

Weight of Cement/Calcium Nitrate mixture ____________ grams

Antifoam Volume ____________ mL

Sodium Silicate ____________ mL

Water to Cement Ratio ____________

Time Sample Produced ____________

Cure Oven Temperature ____________ °C

Cure Time ____________ hours

Solidification Results:

Free Liquid Volume ____________ mL

Physical defects present: Yes No psi

Compressive Strength - 24 hour cure ____________ psi

Observations: (Including pourability, gel time, visual inspection and others as detected.)

Sample prepared by: ____________ Date: ____________

Results Approved: ____________, Manager Analytical Laboratory

Date: ____________

INSERT FIGURE 4

PRESOLIDIFICATION VERIFICATION FLOWCHART

ATTACHMENT A TO SOP 70-33

Copies to: QA upon completion of campaign.

CEMENT SOLIDIFICATION RECIPE INPUT DATA	OSR/TR-IRTS-2
Concentrates Tank (5D15A1 or 5D15A2)	____________
Lab Analysis Log Number (attached)	____________
Batch Size (Gallons)	____________
Minimum Mixer Liquid Weight (lbs)	____________
Maximum Mixer Liquid Weight (lbs)	____________
Minimum Sodium Silicate Weight (lbs)	____________
Nominal Sodium Silicate Weight (lbs)	____________
Maximum Sodium Silicate Weight (lbs)	____________
Percent Water In Waste	____________
Slurry Specific Gravity	____________
Minimum Mix Time (secs.)	____________
Minimum Water/Cement Ratio	____________
Nominal Water/Cement Ratio	____________
V-2 Timer Setting *	____________
Acrison Set Point	____________
Antifoam Pump Timer Setting	____________
NaSi Pump Setting (strokes)	____________

PROCESS CONTROL ENGINEER/DATE ______________________________

VERIFIED BY ______________________________
SS/PCE

* - If V-2 setting is changed to accomodate processing, denote new setting and initial drum affected.

5.9 The CSS Shift Supervisor will be given a copy of the analytical request form showing the performance of the waste form to this point, which will allow processing of the batch of waste.

5.9.1 Shift Engineer reviews all data including gel time, and the following Technical Requirements:

a. TR-IRTS-TBD: Cs-137 concentration TBD
b. TR-IRTS-TBD: -
   - Completion of presolidification testing to ensure compressive strength greater than TBD psi.
c. TR-I TS-TBD CSS Cement Recipe
d. Total Pu: TBD
e. Sulfate SO_4: TBD
f. TDS: TBD

5.9.2 If satisfactory, the Shift Engineer completes the Recipe Input Data Sheet (SOP 70-33).

NOTE:

IF THE COMPRESSIVE STRENGTH OF A CUBE SAMPLE IS BELOW TBD PSI, THEN A VIOLATION OF WVNS TECHNICAL REQUIREMENT OSR/TR-IRTS-8 OCCURS. PROCESSING WILL NOT PROCEED. A CRITIQUE WILL BE HELD TO INVESTIGATE THE CAUSE OF THE LOW COMPRESSIVE STRENGTH, AND ALL WASTE FROM THAT BATCH WILL BE CONSIDERED SUSPECT. A NONCONFORMANCE REPORT WILL AGAIN BE ISSUED.

ALL DRUMS FOUND TO BE OUT-OF-SPECIFICATION WILL BE HANDLED IN ACCORDANCE WITH SECTION 3.3 OF THIS PROCEDURE.

5.13 The gel time of the first full-scale drum from each lot will be verified by visual inspection. If the gel time of the full-scale product is less than 90 minutes, processing may proceed.

If the gel time of a full-scale drum is greater than 90 minutes, the process will be stopped, and an Occurrence Report will be completed per WV-987. Processing may or may not be resumed, based on a technical evaluation of processing variables, including, but not limited to: water-to-cement ratio, source of cement/$CaNO_3$ blend, $CaNO_3$ content in the blend, NaSi addition, etc.

6.0 FULL-SCALE SOLIDIFICATION

6.1 Calculation of Full-Scale Formulation

The constituents for the full-scale recipe on a unit basis are identified in Section 6.2 for decontaminated sludge wash. The recipe is verified for each batch of waste collected following evaporation in 5-D-15A1 or -15A2 as described in Section 4.0 and

5.0. The decontaminated sludge wash solution has been demonstrated to be homogeneous during preoperational testing and the need for recipe changes is considered unlikely. Note that the CSS Waste Dispensing Vessel (400 gallon nominal capacity) is recirculated at 80 GPM. Homogeneity is, however, verified by chemical and radiochemical analyses in conducting routine verification of solidification. Following verification in the laboratory, the Shift Engineer selects a full-scale recipe depending on the batch size to be processed from Tables TBD. These recipes are all based on the standard recipe varying in percent of drum fill only. The recipe utilized is documented in the shift log and during processing; process limits are controlled to within the permitted variance stated in the recipe.

In the event that the sample cannot be solidified using constituents within the allowed recipe variance, full-scale processing is secured and the Operations Manager is notified. Full-scale solidification is not permitted until the recipe is resolved.

6.2 Full-Scale Formulation

The following full-scale reference formula will produce a dry solid monolith capable of performing in accordance with the 10 CFR 61 requirement for stablized LLW. The data are provided for one gallon of waste:

o Decontaminated supernatant (at 20 w/o nominal total dissolved solids)	gallon
o Portland #1 cement with nominally 5.8 w/o $Ca(NO_3)_2$ preblended	pounds
o Silicon Based Antifoam additive GE AF-9020	to mL
o Liquid Sodium Silicate	pounds

6.3 Full-Scale Formulation Control

Laboratory verification of the full-scale formulation is described for each batch of waste to be processed in Section 4.0. Calculation of the recipe based on the laboratory verification is discussed in Section 6.1 and the run plan, attachment A. Process control and full-scale recipe data recording are discussed in Section 3.6. Waste classification is based on the isotopic content of the decontaminated sludge wash as determined by the analytical methods described in Section 5.0 and the total drum weight as recorded in the Data Acquisition System (Section 3.6).

7.0 RECORDS, DOCUMENT CONTROL, AND QUALITY ASSURANCE

Sample verification is performed in the Analytical Laboratory using approved Analytical Procedures and Analytical Methods. Decontaminated sludge wash concentrate samples are withdrawn from either tank 5-D-15A1 or 5-D-15A2 and are delivered to the laboratory for analysis (specific analyses are described in Section 4.0 and 5.0). The sample identification number is assigned by the Analytical Laboratory and is logged in according to sample receiving procedures.

The required analyses are performed (see Sections 4.0 and 5.0) and the data recorded on analytical data sheets for radiochemical anal sis and on the Solidification Data Sheet for sample solidification verif cation. All data sheets are reviewed in accordance with Analytical Ch mistry Procedure, ACP-5.1. All analyses are performed in accordance with approved procedures and under the Analytical Quality Assurance Program.

Copies of the Analytical Data Sheets are delivered to the CSS Shift Supervisor. The Shift Engineer reviews all data and calculates the recipe to be used for the decontaminated waste batch to be processed. The Shift Engineer and CSS Shift Supervisor sign the Recipe Input Data Sheet (SOP 70-33) and attach the corresponding Analytical Request Forms, prior to processing the batch. The Analytical Sample Log number is recorded in the shift log. The recipe is calculated by the shift engineer using the calculation sheet contained in the shift log. The recipe calculation for a single tank's volume of waste will remain unchanged for a normal processing week because of the capacity of the sampled tank (about 5 - 10,000 gallons) and its homogeneity. Since the waste is homogeneous, recipe changes during any processing week are not anticipated, although, slight variation in the recipe within the limits provided in approved recipes (Tables TBD through TBD) is permitted. The recipe calculation is reviewed and approved by the Shift Supervisor if the full-scale recipe is determined to be within the recipe variances allowed. If the recipe is calculated to be outside the allowed variance, full-scale solidification is not permitted to proceed and the Operations Manager is contacted for resolutio

Periodic quality assurance surveil ce of the log book sheets, solid fication operations and ana ical work is performed to assure that the calculations are performed correctly and in accordance with approved proced es.

The Analytical Data Sheets are controlled in accordance with the Analytical Laboratory Document Control Procedures. The operating log book contains uniquely numbered pages for each day of operation. These logs are retained in the shift office during use and are retained by the Plant System Operations Document Control group when completed. All records are available for retrieval if necessary.

Data Acquisition System (DAS) output contains a processing record for each drum produced at CSS. Records are also maintained through the WVDP Master Records Center. Each drum produced is classified by the Waste

Disposal Operations group using radiochemical analysis data as described in Section 5.0 and the drum weight as calculated by the DAS. The waste classification methodology is controlled by Standard Operating Procedure 9-8, Waste Classification. Classification records are retained for each drum by the Waste Disposal Operations group. The DAS output is retained by Operations Document Control in accordance with Standard Operating Procedure 001, "Control of Work Instruction Documents". Individual drum data sheets are transmitted to Waste Disposal Operations in accordance with Standard Operating Procedure 9-2, "Solid Radioactive Waste Disposal". A complete data package for each drum will be maintained in accordance with SOP 70-TBD.

8.0 FULL-SCALE DRUM TESTING

In addition to the sample verification described in Section 4.0 and 5.0, full-scale verification of solidification is also planned. One drum per process tank (based on the observed consistency of the process) will be sampled at random to verify predicted fill as calculated from recipe constituents (see Tables TBD-TBD) absence of any free liquid and penetration resistance following a 3-day cure. The objective of these tests is to confirm successful solidification in the full-scale waste form, confirming the sample solidification results. Deficiencies observed in the full-scale waste will prompt further investigation of drums produced from a given waste batch.

During production of the full-scale waste form, one drum per production process tank is placed into a test fixture located in the Process Cell. The drum is allowed to cure and is inspected for fill height, free liquid and penetration resistance. An Inspection Data Sheet is prepared in accordance with SOP 70-40 inspection procedure and forwarded to Operations in accordance with SOP 00-1, attachment B-1. The testing will be done in accordance with the run plan.

ATTACHMENT A

CEMENT SOLIDIFICATION SYSTEM RUN PLAN FOR SLUDGE WASH LIQUID

TABLE OF CONTENTS

ATTACHMENT A

TABLE OF CONTENTS (continued)

ATTACHMENT A

CEMENT SOLIDIFICATION SYSTEM RUN PLAN

1.0 **INTRODUCTION**

This Run Plan addresses the procedures, equipment, and controls necessary for proper operation of the Cement Solidification System.

2.0 **OBJECTIVES**

The objective of the CSS is to solidify decontaminated sludge wash solution processed by the LWTS with cement to produce a waste form meeting the requirements of 10CFR61.

3.0 **SAFETY**

3.1 **Industrial Safety**

Safe operation of this system is the responsibility of the CSS operating personnel. Control will be effected through the use of approved SOP's.

3.2 **Radiation Safety**

All operations will be performed in accordance with the latest revision of the WVNS Radiological Controls Manual, WVDP-010 and operating procedures.

3.3 **OSR's**

Operation will also be conducted within limits and conditions set by the Operational Safety Requirements. OSR requirements are indicated in the SOP's, shift log data sheets and the Run Plan Graphic (attachment A2) which is posted in the control room.

4.0 **EQUIPMENT**

The following equipment shall be available in the area during CSS operations:

A. Tool box with assorted hand tools

B. Drum pallets

C. Anti-C clothing

D. Respirators

5.0 **REFERENCES**

A. Process Control Plan, WVNS-PCP-002

B. Cement Solidification System Safety Analysis Report, SAR Volume IV

C. Design Criteria

D. Standard Operating Procedures indicated in the following listing:

SOP 70-1	Waste Transfer to CSS
SOP 70-3	Automatic Solidification Operation
SOP 70-4	CSS Manual Solidification with the Process Logic Controller Operational
SOP 70-5	Gravimetric Feeder Operation
SOP 70-6	Bulk Cement Transfer to Dry Bin

ATTACHMENT A (continued)

5.0 **REFERENCES** (continued)

SOP 70-7 Cement Truck Unloading

SOP 70-8 Clean Drum Handling for CSS

SOP 70-9 Automatic Drum Operations for Cement Solidification System

SOP 70-10 CSS Drum/Overpack Handling

SOP 70-11 CSS Manual Operation with Process Logic Controller Nonoperational

SOP 70-12 CSS Mixer System Flush Operation

SOP 70-14 01-14 Building Ventilation System

SOP 70-15 01-14 Building H&V Filter Change

SOP 70-16 Filter Change Room Filter Change

SOP 70-17 Manual Drum Operations for CSS

SOP 70-18 Alarm Procedure for CSS

SOP 70-19 CSS Emergency Procedure Power Failure

SOP 70-25 Calibration Procedure for CSS Gravimetric Feeder

SOP 70-31 CSS Drum Conveyor Alarm Responses

SOP 70-32 Operation of the CSS Silo Air Dryer

SOP 70-33 Data Acquisition System Operation

SOP 70-34 Operation of the 01-14/CSS Process Room 4-Ton Bridge Crane

SOP 70-35 Operation of the Maintenance 2-Ton Bridge Crane

SOP 70-37 Smear Robot Operation

SOP 70-39 Draining and Flushing the Waste Dispensing Vessel

SOP 70-40 Full Size Testing of Solidified Product

SOP 70-41 CSS Preventive Maintenance Program

SOP 70-TBD Waste Certification

Run Plan Graphic Drawings 900D-TBD, Sheets 1 and 2

6.0 WASTE TRANSFERS

Waste transfers to the CSS will be made as required using SOP 70-1. The batch size transferred to the Waste Dispensing Vessel will be approximately 400 gallons, which is enough to produce about ten (10) drums of solidified waste. The waste will be sampled prior to the first transfer at 5-D-15A1 or 5-D-15A2 in accordance with the Process Control Plan. The sample will be assigned a sample log number when it is received at the Analytical Laboratory and will be analyzed for it's chemical and radiochemical composition in accordance with the Process Control Plan. A portion of the sample will be solidified to verify that use of the reference recipe will result in solid dry monolith with appropriate compressive strength. The analysis results and Solidification Data Sheet will be sent to the CSS shift office; using the solidification sample verification data sheet, the shift engineer will select an approved full scale recipe from attachment A1 and document the calculation in the shift log book. Full scale solidification will not be initiated without acceptable verification of solidification in the laboratory.

Due to its larger operating volume, tank 5D15A1 is sampled prior to solidification and at 50 percent ± 10 percent level as an in-process check.

7.0 CSS OPERATIONS

7.1 General System Operations

Prior to initiating transfers to the Waste Dispensing Vessel, verification of solidification for a sample of waste to be transferred and recipe calculation for the full scale product must be completed.

ATTACHMENT A (continued)

7.1.1 Waste may be transferred to the Waste Dispensing Vessel from either Concentrates Storage Tanks 5-D-15A1 or 5-D-15A2 while the solidification process is ongoing provided that solidification verification was performed on a sample of the waste being transferred prior to initiating the transfer. Transfers are made just prior to reaching the low level alarm point in the Waste Dispensing Vessel. At that point, sufficient volume remains in the Waste Dispensing Vessel to continue processing for 40 minutes. Three (3) or four (4) transfers will be required per shift. Waste transfers are performed in accordance with SOP 70-1

7.1.2 Drums will be tested for surface contamination prior to release to the Drum Loadout Area. Drums released to the Drum Loadout Area must have smearable surface contamination levels less than 50 dpm/100 cm^2 Alpha and less than 500 dpm/100 cm^2 Beta contamination. All drums with greater amounts of removable contamination will be decontaminated. Contamination testing of packages is performed in accordance with SOP 70-37. The top, sides, and bottom will be tested.

7.1.3 Two (2) mixers will normally be used for waste processing using SOP 70-3.

7.1.4 Prior to any extended shutdown of the process, the mixers will be flushed to a decant drum using SOP 70-12.

7.1.5 As eight (8) drums are staged in the Drum Loadout Area, the drums will be loaded out by Waste Operations and transported to the RTS Drum Cell. All drums will be labeled with an individual bar code serial number. All drum data: production recipe, date filled, weight, dose rate, surface contamination

ATTACHMENT A (continued)

level, etc., will be cross referenced to this bar code serial number and recorded by the Data Acquisition System (DAS). Drum production records as recorded by the DAS will be retained by Operations Document Control in accordance with SOP 00-1. Individual drum data sheets are transmitted to Waste Operations in accordance with SOP 9-2.

7.1.6 All drum records including processing data, waste classification data sheets, and DAS data will be compiled into a waste certification package in accordance with SOP 70-TBD.

7.2 **Waste Recipe**

The decontaminated sludge wash solution will be solidified in the CSS in accordance with CSS SOP's. The approved recipes are shown in Table 1. Recipe verification is discussed in Section 6.0. As an operator aid, a graphic is included in attachment A2 showing the process flow, process procedures, operational safety requirements, product quality requirements and process requirements.

7.3 **Mixer Flushing and Flush Processing**

Flush operations will be conducted using SOP 70-12.

7.4 **System Flushing**

If necessary for maintenance, the system may be flushed.

7.4.1 The Waste Dispensing Vessel is flushed and drained in accordance with SOP 70-39.

7.4.2 The mixers are flushed in accordance with SOP 70-12.

7.5 Conduct of Operations

A Shift Engineer and a CSS Shift Supervisor will be on each shift to assure safe and technically correct operation of the Cement Solidification System. Technical direction of the work is the responsibility of the Shift Engineer, all direction provided to the operators or Maintenance personnel will be made through the CSS Shift Supervisor.

In the event of any casualty or emergency situation, the CSS Shift Supervisor, by virtue of training and experience, is solely responsible to direct any actions necessary to stop and recover from such situations.

Full recovery from any casualty or emergency situation will performed in accordance with established emergency procedures.

8.0 RESPONSE TO EMERGENCIES

Should a fire, or other emergency requiring evacuation occur during processing operations, the operating personnel should take the following steps:

8.1 Waste Transfer

Immediately stop the operation in accordance with SOP 70-1 and follow plant emergency procedures.

8.2 Waste Processing in Automatic

Allow the batch to continue in accordance with SOP 70-3. The system will finish the batch and stop when an empty drum is not transferred to the Fill Station. Follow plant emergency procedures.

8.3 **Waste Processing in Manual**

Discharge mixers to drum in accordance with SOP 70-11, follow plant emergency procedures.

8.4 **Flushing or Flush Processing**

Immediately stop the operation in accordance with SOP 70-12 and follow plant emergency procedures.

8.5 **Drum Smearing and Loadout**

Immediately stop the operation in accordance with SOP 70-37 and follow plant emergency procedures. Note that if the Drum Loadout Shield Door is **OPEN**, any drums should be indexed clear of the shield door, the truck drawbridge should be raised, and the shield door should be **CLOSED**.

8.6 **LOSS OF VENTILATION**

Allow the batch to complete per SOP 70-3 (Automatic) or SOP 70-11 (Manual). Do not resume operation until ventilation has been restored in accordance with SOP 70-14. Evacuation of the CSS Control Room is not required.

8.7 **LOSS OF ELECTRIC POWER**

Complete the batch and initiate flush in accordance with SOP 70-19. Evacuation of the CSS Control Room is not required.

9.0 QUALITY ASSURANCE AND RECORDS MANAGEMENT

9.1 Sample Verification Data Sheets

Sample verification is performed for each tank volume 5-D-15A1 or 5-D-15A2 feeding to the CSS Waste Dispensing Vessel to assure proper solidification of the waste using the reference recipe. Copies of the solidification sample data sheets are sent to Process Control Engineering. Data sheets are approved in accordance with Analytical Chemistry Procedure ACP-5.1.

9.2 Log Book Records

A daily log book, one set of uniquely numbered entry pages per day, is maintained at the CSS shift office. The log book is used for data recording required by procedure and for documentation of the recipe used. The log book contains the sample solidification verification log number assigned for each feed tank of waste to be processed 5-D-15A1 or 5-D-15A2 by the Analytical Laboratory as a reference. Log book entries are reviewed and approved by the CSS shift supervisor and when completed for an operating year, are submitted to the Master Record Center for retention

9.3 Waste Certification

DAS output contains production data for each drum processed at CSS. The DAS weekly activity file is maintained on disk. Drum records may be copied to diskette during nonoperational periods.

Manual data recorded on SOP 70-4, attachment B, and DAS Real Time Printout are reviewed by Process Control Engineering and forwarded to Quality Assurance with transmittal sheet. SOP 70-33, attachment B.

ATTACHMENT A (continued)

A copy of Presolidification Test Data, Analytical Request Form WV-1113, is forwarded from Analytical & Process Chemistry to Quality Assurance and Disposal Operations.

Missing data or data requiring clarification is corrected by Process Control Engineering and Quality Assurance. Revisions to the Drum Data Base are recorded and authorized on attachment C to SOP 70-33.

Final drum classification, based on drum data and radiochemical analysis is completed by Analytical and Process Chemistry in accordance with SOP 9-8, "Waste Classification" and verified by Waste Engineering.

All drum data, including: drum classification and processing data, are compiled by Process Control Engineering per SOP 70-TBD.

9.4 **Full Scale Drum Testing**

From each Processing Tank 5-D-15A1 or A2, a drum is pulled at random from the production line and is placed into the drum test fixture located in the process room. The drum is tested to assure proper fill, proper penetration resistance and dryness with respect to free liquids as required in SOP 70-40.

ATTACHMENT A (continued)

10.0 PREVENTIVE MAINTENANCE AND CALIBRATIONS

10.1 Preventive Maintenance

Periodic preventive maintenance required for the CSS is described in SOP 70-41, periodic preventive maintenance items are scheduled in the maintenance recall system.

10.2 Calibrations

Instruments requiring periodic calibration are identified in the appropriate maintenance recall lists.

ATTACHMENT A1

REFERENCE RECIPES FOR SLUDGE WASH LIQUID

ATTACHMENT A2

RUN PLAN GRAPHIC

Waste Form Interim Qualification Report
WVDP Stabilized Sludge Wash Cement-Waste

Table of Contents

1.0 INTRODUCTION

This document is presented by West Valley Nuclear Services Co., Inc. (WVNS) to provide technical information on a stabilized (Class A, B, or C) cement-waste form to be produced at the West Valley Demonstration Project (WVDP). The information is intended to show compliance to the requirements for radioactive low-level waste (LLW) as set forth in 10 CFR 61, supplemented by the 1991 US NRC Technical Position paper (TP).

2.0 BACKGROUND

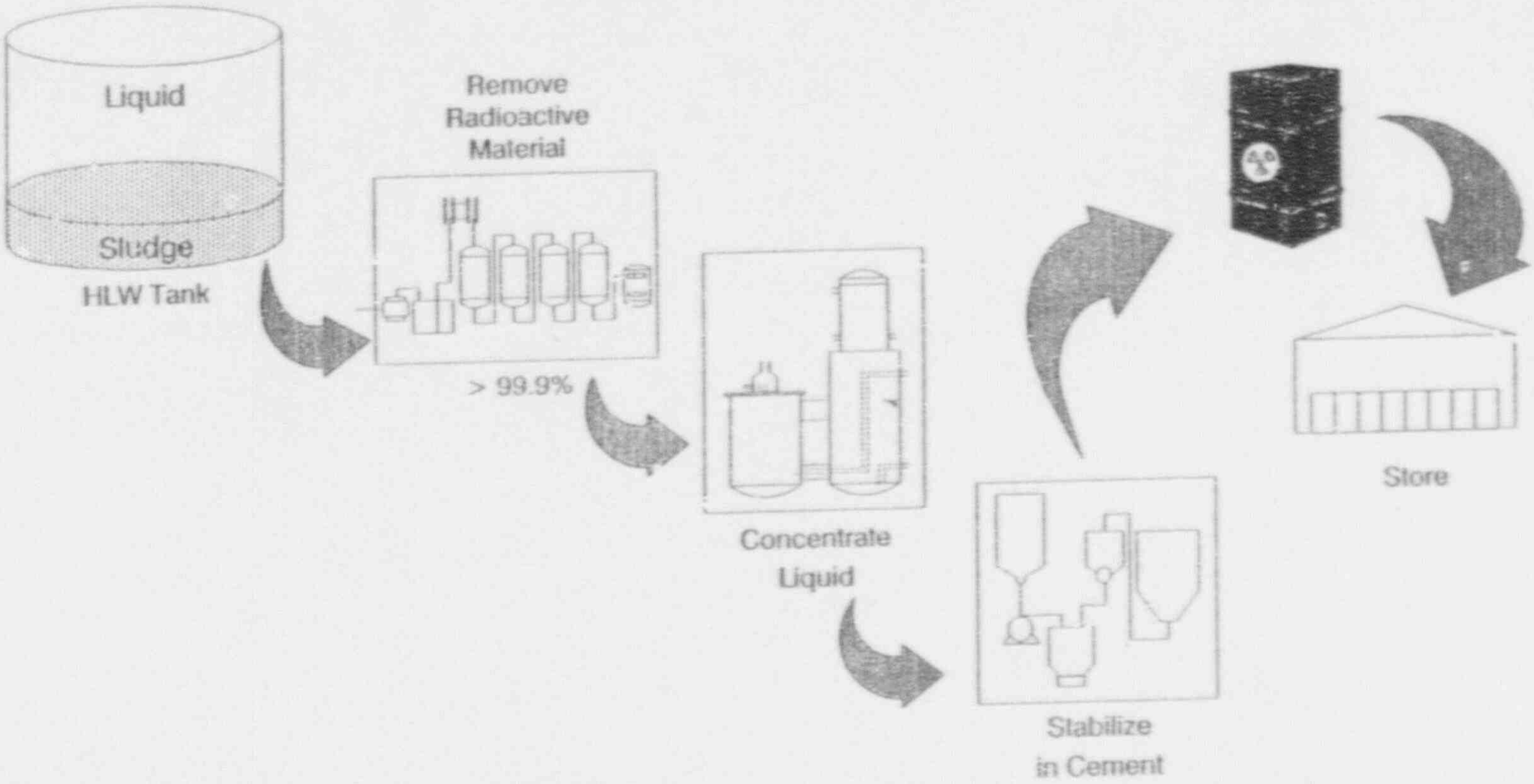
The West Valley Demonstration Project Act of October 1, 1980 (Public Law 96-368) directs the Department of Energy (DOE) to carry out a radioactive high-level waste (HLW) management demonstration project at the West Valley, New York site. The West Valley site was the location of the only operating commercial nuclear fuel reprocessing plant in the United States. West Valley Nuclear Services Co., Inc., a subsidiary of Westinghouse Electric Corporation, has been the prime contractor to DOE for site operations since 1982.

The demonstration project will remove HLW from underground storage tanks and solidify it into a borosilicate glass for long-term storage at a future federal repository. The major portion of the HLW amounted to about 2 million liters of fluid stored in an underground storage tank, designated Tank 8D-2. The tank also contained a sludge layer on the floor of the tank that had insoluble oxides, hydroxides, and carbonates of many species (principally iron). Also in the sludge layer was undissolved sodium sulfate crystals that precipitated from the supernatant liquid.

Prior to HLW stabilization in borosilicate glass, several pretreatment operations were defined that would minimize the final volume of HLW glass. Beginning in 1988, WVNS processed the liquid supernatant solution from Tank 8D-2 through an ion-exchange process to yield a LLW solution (Figure 1). The LLW stream was concentrated and made into a cementicious waste form. The Class C cement-waste is described in a previous topical report "Cement Waste Form Qualification Report - WVDP PUREX Decontaminated Supernatant". Cement-waste drums were made up through November, 1990.

A new pretreatment step is being implemented at the WVDP. The HLW in Tank 8D-2 is being mobilized by five pumps, which allows the sodium sulfate crystals to dissolve into the sludge wash water. By adding caustic during the sludge washing operation, uranium, strontium, and plutonium will be maintained at trace levels in the sludge wash solution.

High-Level Waste Pretreatment



The resulting sludge wash solution will be treated in the ion exchange process as was done with the p:evious supernatant solution. A ew ion exchange zeolite will be used to retain cesium, strontium, and plutonium from the sludge wash solution. The resulting LLW stream will be concentrated and made into a cementicious waste form similar to previous supernatant cement-waste in the Cement Solidification System (CSS).

Depending on the level of plutonium, strontium, and cesium after ion-exchange, the cement-waste may be classified as A, B or C waste forms. Class A can be achieved because of the trace levels of strontium and plutonium from the sludge wash process, the new ion exchange zeolite to retain strontium and plutonium, and the lower weight percent salt content in the final LLW stream (compared to the supernatant process).

By choosing to qualify the waste form as stabilized, any class cement-waste may be produced. In doing so, WVNS acquires an option on the final disposal of this new waste form. If deemed appropriate, these new cement-waste forms may be disposed in conjunction with the previous supernatant Class C cement-waste material.

3.0 WASTE CHARACTERIZATION

The LLW stream for which data are presented to demonstrate qualification is sludge wash solution with 20 wt% dissolved salts. The candidate waste has the following characteristics:

Major Constituents:	Nominal 20 wt% salt solution composed primarily of sodium, nitrate, nitrite, and sulfate salts (about 95% of the total salts)
Density:	Nominal 1.15 - 1.16 g/ml
Temperature:	Ambient - 90°F
Secondary Species:	Laboratory-generated sludge wash solution and preliminary Tank 8D-2 actual sludge wash compositions are depicted in Table 1. Non-radioactive surrogate solutions for qualification testing are shown in Table 2.

Table 1

Chemical Composition of
Laboratory-Generated Sludge Wash Solution
& Preliminary Actual Sludge Wash Solution

	Laboratory		Tank 8D-2	
	Dry Wt%	g/l	Dry Wt%	g/l
Major:				
Na	31	75	31	69
NO_3	27	66	28	63
NO_2	23	56	25	56
SO_4	10	25	10	23
Minor:				
K	1.2	3.0		
Al	0.52	1.3	0.13	0.30
Cl	0.20	0.49	0.21	0.49
Ca*	0.20	0.48		
B	0.16	0.39		
P	0.15	0.37		
Cr	0.11	0.26		
Fe*	0.053	0.13		
U*	0.0071	0.017	0.0020	0.0048
pH	12.2		12.5	

* not used in surrogate solution

Table 2

Chemical Composition of
Surrogate Sludge Wash Solutions
For Cement-Waste Qualification Tests

	Original Surrogate Dry Wt%	Original Surrogate g/l @20% TDS	Future Surrogate Dry Wt%	Future Surrogate g/l @20% TDS
Major:				
Na	31	73	30	71
NO_3	27	62	26	62
NO_2	22	51	24	56
SO_4	14	33	9.6	23
CO_3	2.6	5.9	2.8	6.6
Minor:				
K	0.85	2.0	1.1	2.7
Cl	0.21	0.49	0.21	0.49
Cr	0.15	0.35	0.16	0.38
P	0.057	0.13	0.20	0.48
TOC	0.042	0.097	0.045	0.11
Mo	0.024	0.056	0.026	0.062
B	0.0037	0.0087	0.17	0.39
Al	---	---	0.13	0.30

TOC = Total Organic Carbon

Table 3

Trace Chemicals Expected in
Sludge Wash Solution

	Dry ppm	g/l
F	187	0.044
Sn	60	0.014
Rb	53	0.012
Te	34	0.0080
Si	18	0.0042
Se	5	0.001
Cu	2	0.0004
Sr	1	0.0003
Li	1	0.0003
Mg	<1	

Calculated from previous characterization work of supernatant solution [Reference 3]

Other trace species that are expected in the sludge wash solution based on previous HLW supernatant characterization are shown in Table 3.

Analyses of the actual decontaminated sludge wash solution will be provided at a later date.

Radioisotopes: Key radionuclides for laboratory-generated decontaminated sludge wash solution are shown in Table 4.

Other trace radionuclides that are expected in the sludge wash solution based on previous HLW supernatant characterization are shown in Table 5.

Analyses of the actual decontaminated sludge wash solution will be provided at a later date.

4.0 MINIMUM REQUIREMENTS OF 10 CFR 61.56(a)

Section 61.56(a) of 10 CFR Part 61 contains the minimum requirements for all classes of waste. The following sections summarize the different criteria and how the proposed waste form will meet those criteria.

4.1 Packaging

Criteria: The waste form must not be packaged for disposal in cardboard or fiberboard boxes.

Waste Form: The waste form will be poured into plastic-lined 268 liter square 16 gage steel containers as shown in Figure 2.

4.2 Liquid Waste

Criteria: The liquid waste must be solidified or packaged in sufficient absorbent material to absorb twice the volume of the liquid.

Waste Form: The 20% salt solution will be made into a cementicious material with no free liquid.

Table 4

Key Radionuclides in
Decontaminated Sludge Wash Solution

	Measured Value μCi/g solution	Calculated For Cement-Waste with 20% TDS LLW Ci/m^3
Tc-99*	0.284	0.19
Sr-90**	0.00048	0.00032
Cs-137**	0.27	0.18
alpha Pu**	0.012	0.90 nCi/gm

*Measured in actual Tank 8D-2 sludge wash solution

**Measured near a column change in laboratory sludge wash experiment; corrected to 20% total solids (TDS).

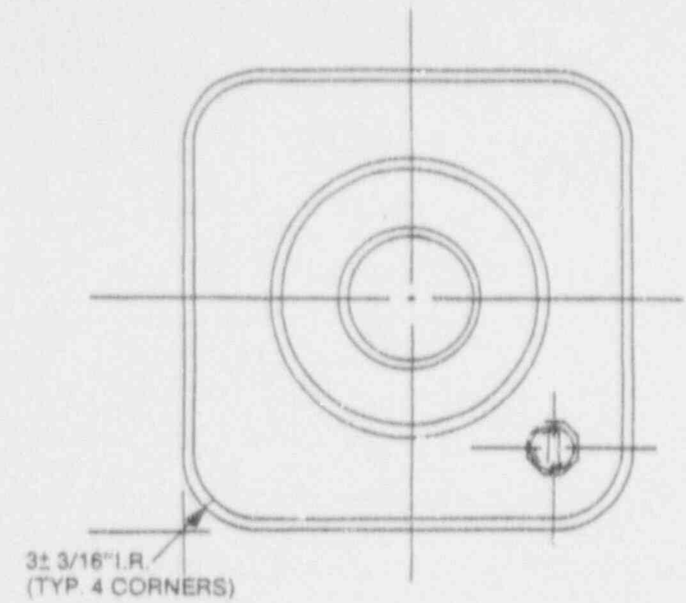
Table 5

Trace Radionuclides Expected in
Decontaminated Sludge Wash Solution

	As of 4/1/92 Ci Ratio Relative to Tc-99	Relative to Cs-137	Cement-Waste @20% TDS mCi/m3
H-3	0.047	---	8.9
C-14	0.086	---	16
Ni-63	0.54	---	102
Se-79	0.023	---	4.4
Zr-93	0.00014	---	0.027
Nb-93m	0.000065	---	0.012
Ru-106	0.000034	---	0.0064
Rh-106	0.000034	---	0.0064
Pd-107	7.5E-06	---	0.0014
Cd-113m	0.010	---	1.9
Sn-121m	8.7E-07	---	0.00016
Sb-125	0.011	---	2.0
Te-125m	0.0024	---	0.46
Sn-126	0.00025	---	0.048
Sb-126m	0.00025	---	0.048
Sb-126	0.00010	---	0.019
I-129	0.00013	---	0.025
Cs-134	---	0.00043	0.077
Cs-135	---	0.000024	0.0043
Ce-144	2.7E-10	---	<0.0000001
Pr-144	2.7E-10	---	<0.0000001
Pm-147	0.030	---	5.6
Sm-151	0.00066	---	0.13
Eu-152	0.000021	---	0.0039
Eu-154	0.0057	---	1.1
Eu-155	0.00074	---	0.14

Tc-99 calculated to be 0.19 Ci/m3
Cs-137 assigned to be 0.18 Ci/m3

Calculated from previous characterization work of supernatant solution [Reference 3]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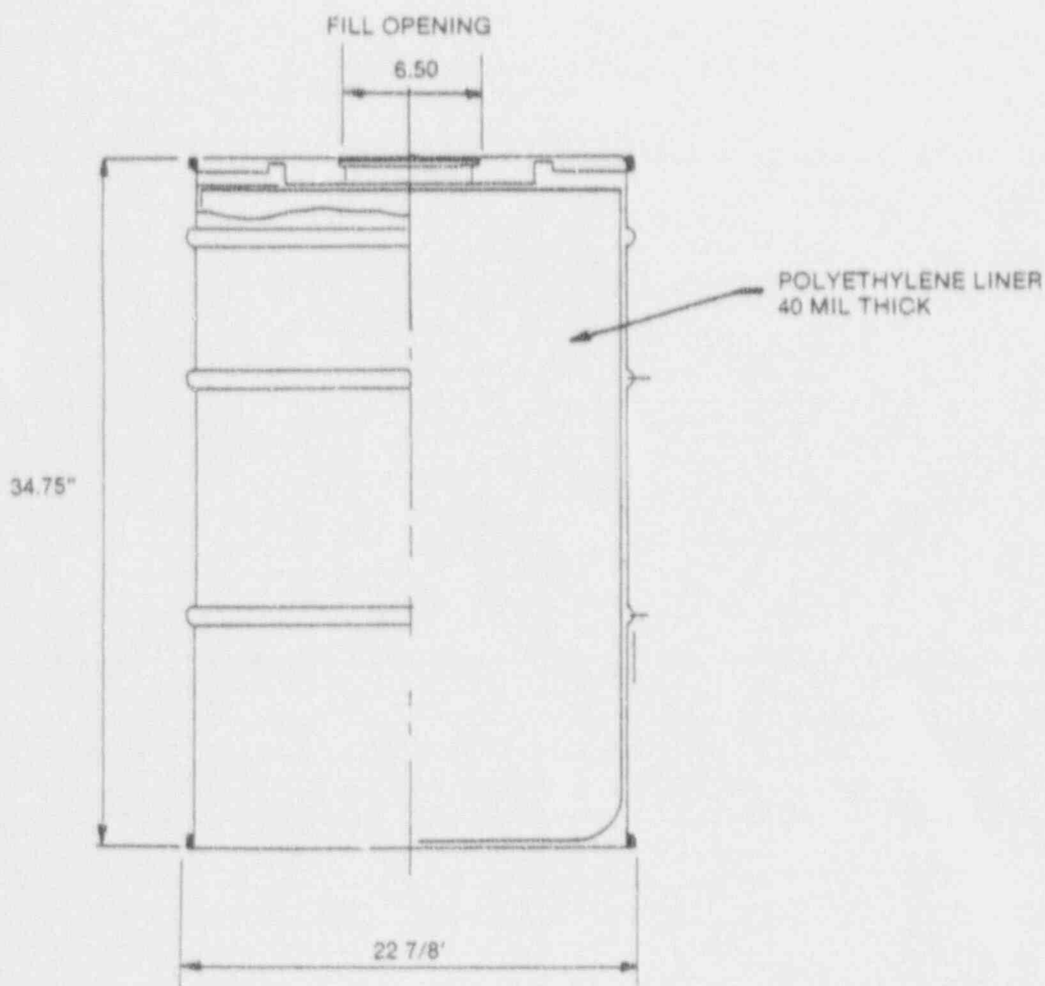
(TYP. 4 CORNERS)


FILL OPENING
6.50
POLYETHYLENE LINER
40 MIL THICK
34.75"
22 7/8'

4.3 <u>Free Liquid</u>

Criteria: Free standing liquid in the solid waste shall not exceed 1% of the solid volume.

Waste Form: Cement-waste product made ith surrogate sludge wash solution has demonstrated no free liquid within one hour after creation of the cementicious material.

4.4 <u>Reactivity of Product</u>

Criteria: The waste must not be readily capable of detonation or of explosive decomposition or reaction at normal pressure and temperatures, or of explosive reaction with water.

Waste Form: After solidification, the waste form will not contain any substances capable of such reactions.

4.5 <u>Gas Generation</u>

Criteria: The waste must not contain or be capable of generating toxic gases, vapors, or fumes harmful to persons transporting, handling or disposing of the waste form.

Waste Form: After solidification, the waste form will not contain any substances capable of such gas releases.

4.6 <u>Pyrophoricity</u>

Criteria: The waste must not be pyrophoric or contain material which are pyrophoric as defined in 20 CFR 61.4.

Waste Form: The waste form does not contain any pyrophoric materials.

4.7 <u>Gaseous Waste</u>

This provision is not applicable to a solidified waste form.

4.8 Hazardous Waste

Criteria: Waste containing hazardous, biological, pathogenic, or infectious material must be treated to reduce the potential hazard.

Waste Form: Chromium in the LLW salt solution is at a level to be considered hazardous per applicable EPA guidelines. After solidification, the chromium will be readily retained in the cement matrix.

Results of TCLP testing of actual radioactive sludge wash cement-waste will be provided at a later date.

5.0 STABILITY REQUIREMENTS OF 10 CFR 61.56(b)

Section 61.56(b) of 10 CFR Part 61 contains the stability requirements for stabilized waste forms. Two of the criteria, structural stability and free liquids, are specifically addressed in the Technical Position paper (TP). Section 6 covers the recommendations of the TP and the data supporting the stabilized cement-waste form.

The other criteria in this section of the regulations cover the void spaces within the waste and between the waste and its package. The steel drums that will contain the processed cement-waste will be filled while the waste form is still fluid. As a result, the void space between the waste and the containers are minimized to the maximum extent possible. Also, specific directions are provided in the Process Control Plan to ensure at least an 85% fill of a drum.

6.0 REQUIREMENTS OF 1991 TECHNICAL POSITION PAPER

The Technical Position paper (TP) contains recommendations on the stability requirements for all classes of stabilized waste. The following sections summarize key criteria from the TP, including Appendix A. Results of testing are presented to show that the waste form meets the criteria.

Two different sets of results are cited in this section. Where available, test results for the proposed waste form (cement-waste made with 20 wt% TDS surrogate sludge wash solution) are presented. Some results are not available for the waste form made from 20% TDS sludge wash solution. For these cases, results from an alternate waste form, cement waste made with sludge wash solution concentrated to 33 wt% dissolved salts, are presented. Additional testing for these cases is also identified and summarized in section 7.3.

6.1 Compressive Strength

Criteria: Sufficient specimens (at least 10) shall be compression tested after a minimum cure time of 28 days. Average compression strength greater than 500 psi is required. Testing shall also be performed to determine the compressive strength increase with time to ensure that the specimens have attained near-maximum compressive strength.

Waste Form: Cores (2 5/8" diameter x 5 1/4" length) were removed from cement-waste drums prepared with non-radioactive surrogate sludge wash solution over the period of several weeks. Results are shown in Figure 3.

Lines representing the 95% confidence interval of the regression line through all the data are provided. The waste-form does not show any statistically significant strength increase beyond 28 days of curing. The average of all the cores is 1247 psi, well in excess of the 500 psi minimum.

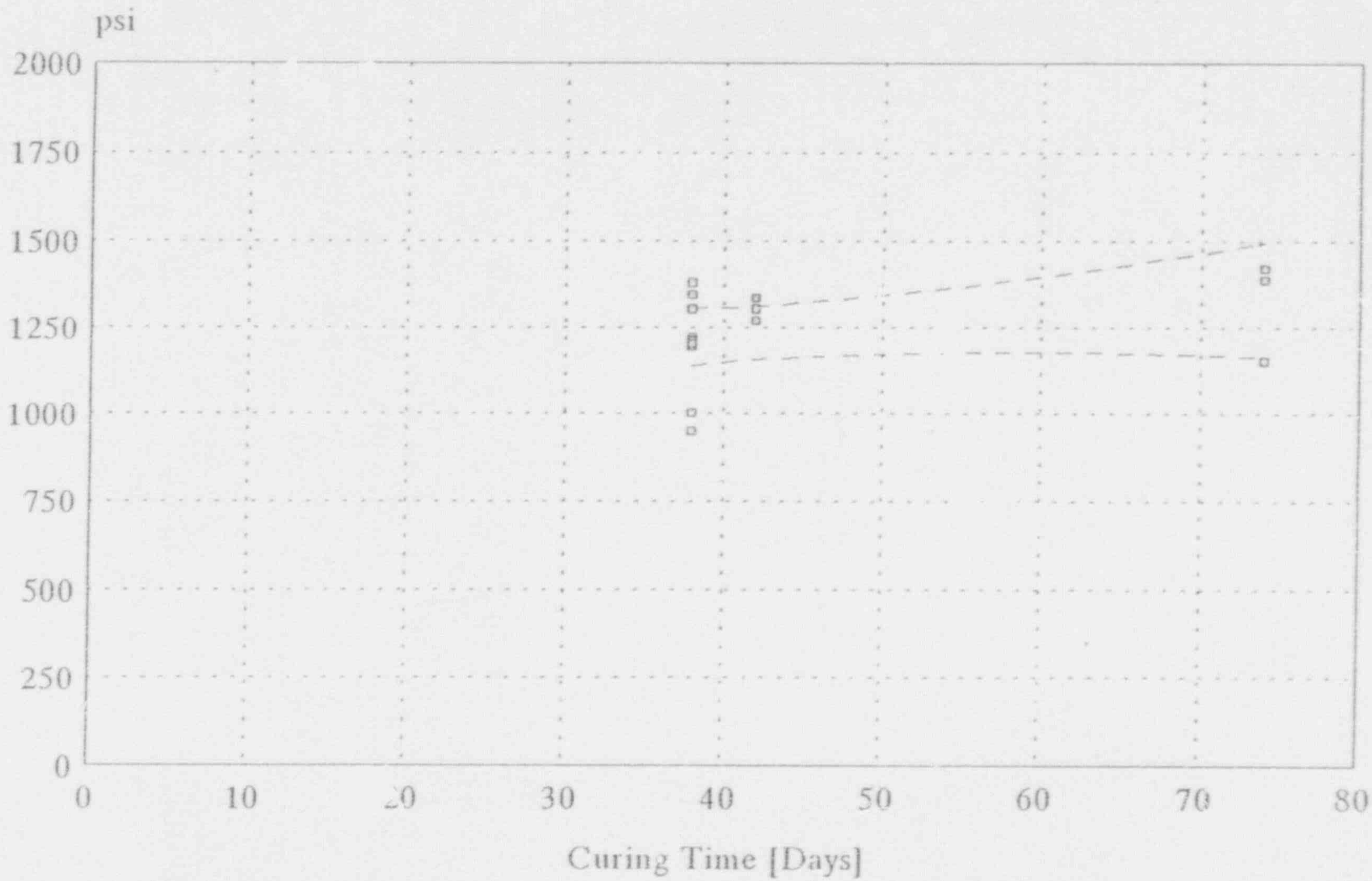
6.2 Radiation Resistance

Waste forms containing ion-exchange resins or other organic materials shall be tested for radiation stability. The proposed WVNS waste form does not contain any ion-exchange resin and only trace quantities of organic materials, thus this test is not required.

6.3 Biodegradation Resistance

Waste forms containing carbonaceous materials shall be tested for biodegradation resistance. The proposed WVNS waste form does not contain appreciable carbonaceous materials, thus this test is not required.

Cured Cement Strength vs Curing Days
Cores from Drums made with 20 wt% Surrogate Solution



Average = 1247 ± 76 psi (95% confidence of mean)

6.4 **Leachability**

Criteria: Leach testing in accordance with ANSI/ANS-16.1 shall be performed on the waste form. Five day tests in both demineralized water and synthetic sea water shall be completed on the cement-stabilized waste form. Leach indices, as calculated per the ANSI/ANS method, shall be greater than 6.0.

Waste Form: The proposed waste form is a stabilized cement-waste made with sludge wash solution at 20% total dissolved salts (TDS). Prior research with the same wash solution, but concentrated to 33% TDS was performed.

Radioactive solution from the HLW tank was collected prior to washing of the HLW sludge. The sample was pH adjusted and supplemented with sodium sulfate to simulate the anticipated sludge wash solution. Mini-cylinders 1" diameter x 3" length were prepared in the laboratory.

The results of the leachability testing are shown in Tables 6 and 7 as well as Figures 4 and 5. The lowest leach index for any of the key radionuclides was 7.69 for Tc-99 in demineralized water leachant.

These positive results at the higher salt loading are suggestive of similar success at the lower salt loading. WVNS will perform leachability testing of cement-waste made with actual sludge wash solution at the lower TDS loading. Results will be reported at a later date.

6.5 **Immersion Resistance**

Criteria: Waste specimens shall be immersed for 90 days in the more aggressive leachant identified in the leachability test. Visual examination of the immersed samples shall be performed to verify no significant degradation (e.g. cracking or spalling). The average compression

Table 6

Leachability Testing Results
Lab-Prepared 33% TDS Mini-cylinders

In Demineralized Water
Average Leachability Index

hrs	Tc-99	Sr-90	Cs-137	α Pu
2	7.725	10.026	7.813	14.047
7	7.831	9.974	8.051	14.219
24	7.692	10.080	7.976	14.224
48	8.112	10.355	8.457	12.961
72	8.555	10.895	8.910	13.083
96	8.936	10.985	9.324	13.186
120	9.299	11.313	9.681	13.269

In Synthetic Sea Water
Average Leachability Index

hrs	Tc-99	Sr-90	Cs-137	α Pu
2	7.855	10.424	7.977	11.751
7	8.010	10.726	8.289	11.924
24	7.797	11.392	8.060	13.235
48	8.026	10.750	8.393	11.153
72	8.459	10.637	8.847	11.682
96	8.879	11.509	9.225	11.783
120	9.138	11.783	9.598	12.106

More Aggressive Leachant

hrs	Tc-99	Sr-90	Cs-137	α Pu
2	Demin	Demin	Demin	Sea
7	Demin	Demin	Demin	Sea
24	Demin	Demin	Demin	Sea
48	Sea	Demin	Sea	Sea
72	Sea	Sea	Sea	Sea
96	Sea	Demin	Sea	Sea
120	Sea	Demin	Sea	Sea

Table 7

Leachability Testing Results for Tc-99
Lab-Prepared 33% TDS Mini-cylinders

Leach Indices
Triplicate Measurements for Tc-99

hrs	Demineralized Water			Synthetic Sea Water		
2	7.716	7.743	7.718	8.091	7.781	7.785
7	7.894	7.782	7.816	8.016	7.991	8.024
24	7.765	7.640	7.672	7.815	7.781	7.794
48	8.074	8.122	8.141	7.985	8.053	8.040
72	8.588	8.490	8.587	8.430	8.508	8.439
96	8.919	8.954	---	8.892	8.866	---
120	9.246	9.280	9.370	9.170	9.131	9.114

Statistical Comparison of Leach Indices for Tc-99
Difference Between Demineralized and Synthetic Sea Water?

	Demin Water		Sea Water			Signif	
hrs	Avg	Var	Avg	Var	Delta	Level	Diff?
2	7.73	0.00015	7.89	0.02108	0.16	0.29	No
7	7.83	0.00220	8.01	0.00020	0.18	0.10	Yes
24	7.69	0.00281	7.80	0.00020	0.10	0.11	No
48	8.11	0.00079	8.03	0.00087	0.09	0.08	Yes
72	8.56	0.00211	8.46	0.00121	0.10	0.11	No
96	8.94	0.00031	8.88	0.00017	0.06	0.07	No
120	9.30	0.00274	9.14	0.00055	0.16	0.11	Yes

Var = variance of replicate measurements

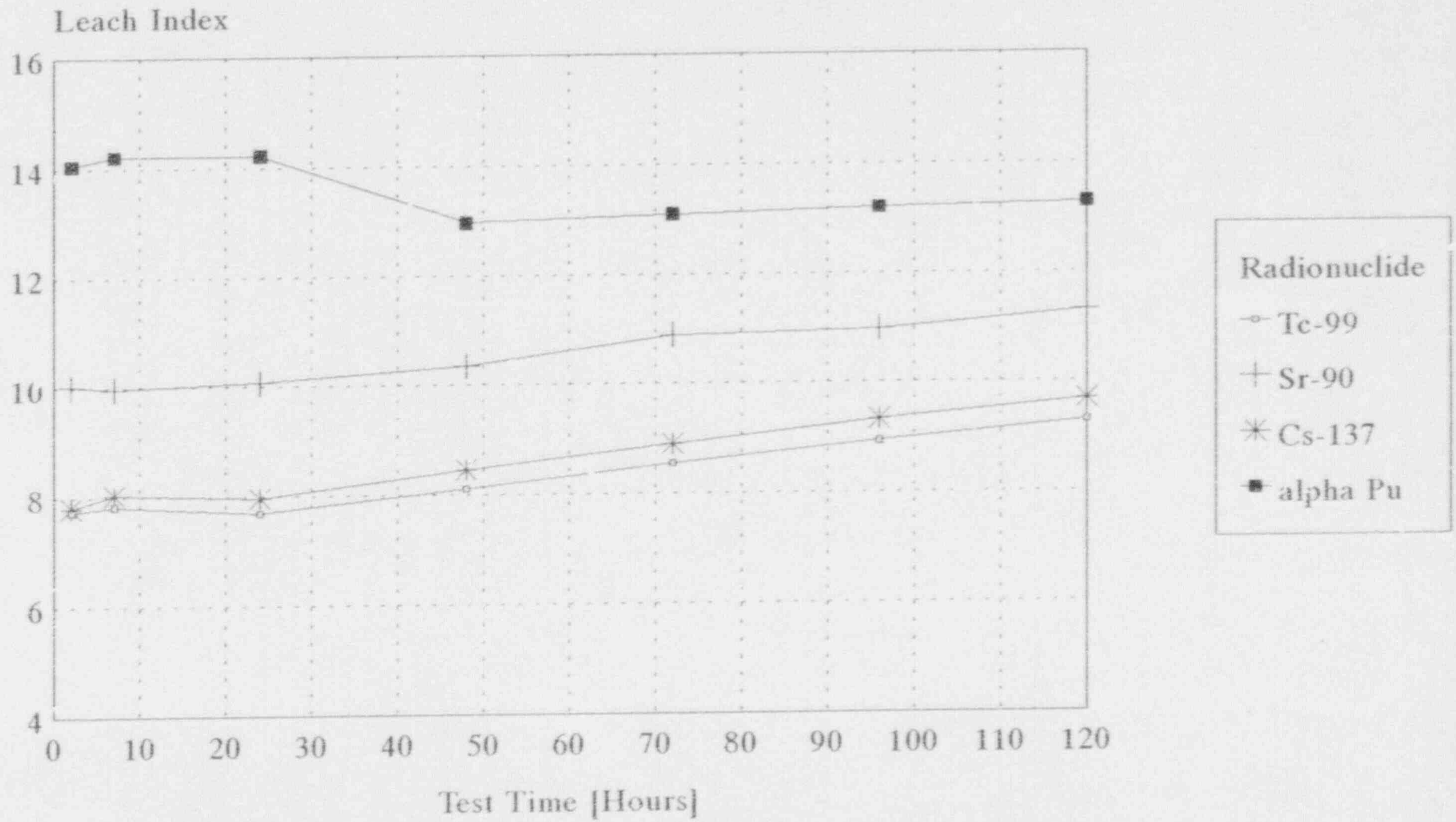
Delta = difference between averages

Signif Level = 95% confidence value for differences between the two averages

Diff = Is delta more than the significance level?

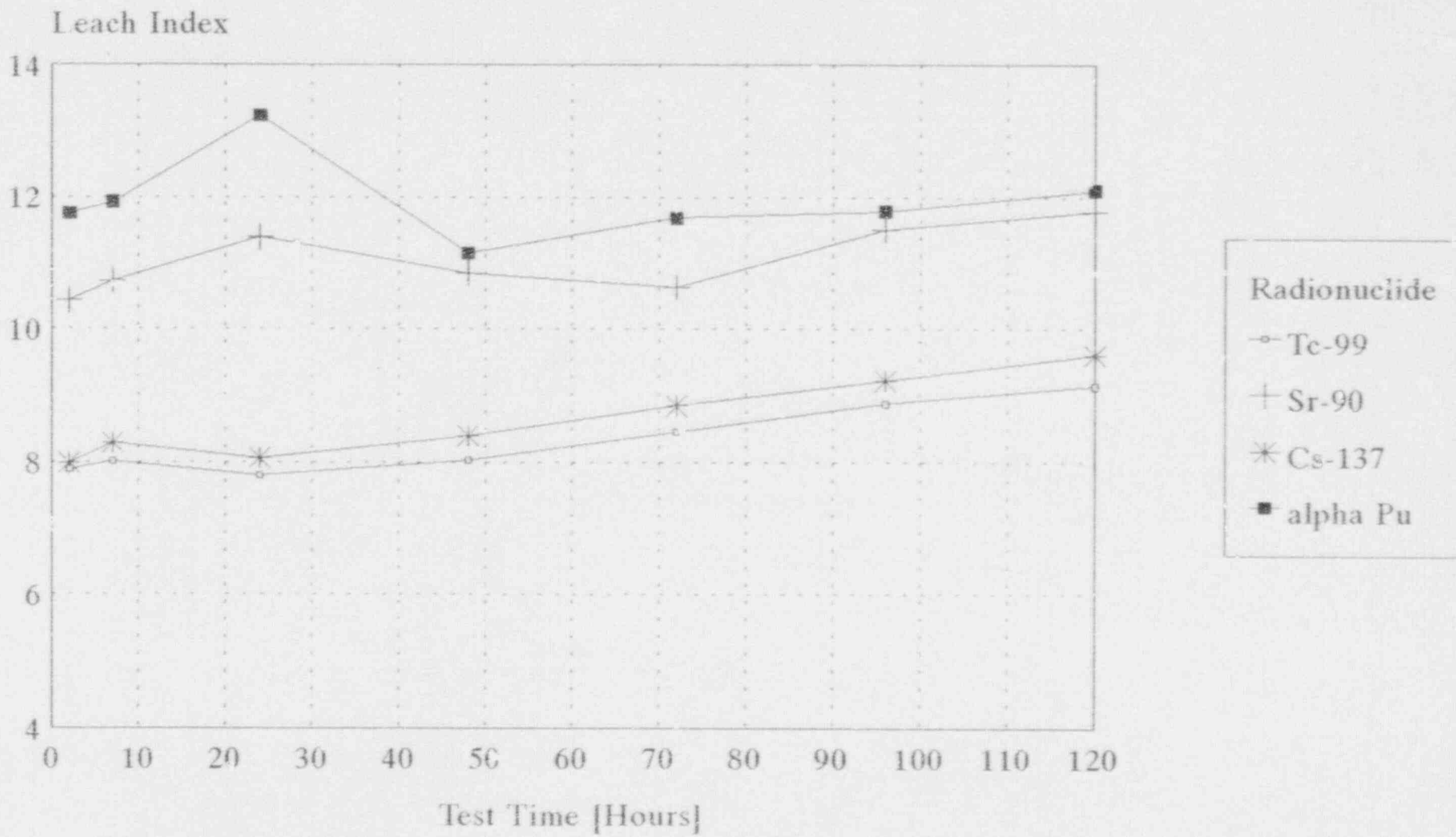
Conclusion: During 5-day test, only subtle differences can be detected for the Tc-99 leach indices in demineralized water and synthetic sea water.

Leachability Indicies
Demineralized Water



Simulated Cement-Waste from 33% TDS solution

Leachability Indicies
Synthetic Sea Water



Simulated Cement-Waste from 33% TDS solution value after immersion shall be greater than 500 psi and more than 75% of the un-immersed baseline average.

For those waste forms that lose more than 25% of the compressive strength compared to the un-immersed average, additional immersion testing through 180 days shall be completed. Sufficient samples shall be tested to show a stabilization of the compression strength by 180 days of immersion. Visual examination of the immersed samples shall be performed to verify no significant degradation (e.g. cracking or spalling). The average compression value after immersion shall be greater than 500 psi.

Waste Form: Cores (2 5/8" diameter x 5 1/4" length) were removed from full-scale cement-waste drums prepared with non-radioactive surrogate sludge wash solution. Three cores were placed into demineralized water and three into synthetic sea water.

After 90 days of immersion, the specimens showed only minor cracking. Average compression strength after immersion was 1722 psi for demineralized water and 1189 psi for synthetic sea water. Compared to the un-immersed baseline average of 1247 psi these represent an increase of over 30% and a decrease of under 5%. Based on these results, the proposed waste form made with 20 wt% TDS sludge wash solution meets this criteria.

As noted in 6.4, prior research with the same LLW stream, but concentrated to 33% TDS was performed. Cores of cement-waste drums made with surrogate solution were immersed in demineralized water. Sulfate attack of the waste form was significant. After 90 days immersion, compressive strength was less than 75% of the un-immersed average. By 120 days of immersion, the strength had fallen below 500 psi. Significant spalling and cracking of the waste form was noted.

Failure of the cement-waste form in this test lead to the investigation of reduced salt loading in the waste form. A reduction of the waste loading by using sludge wash solution concentrated to 20% TDS yields excellent immersion resistance performance.

WVNS will perform additional immersion resistance testing to evaluate the significance of wt% TDS, water-to-cement ratio, and sulfate level in the LLW. Results from these tests will be reported at a later date.

6.6 Thermal Cycling

Criteria: Waste specimens shall be subjected to thirty thermal cycles between -40°C and 60°C in accord with ASTM B553. Visual examination of the cycled samples shall be performed to verify no significant degradation (e.g. cracking or spalling). The average compression value after cycling shall be greater than 500 psi.

Waste Form: As noted in 6.4, prior research with the same LLW stream, but concentrated to 33% TDS was performed. Non-radioactive simulated sludge wash solution was used in the full-scale equipment to fill drums with the cement-waste.

Cylindrical molds (3" diameter x 6" length) were filled with the cement-waste by scooping material directly from the waste drum. One special mold was equipped with a thermocouple along the centerline. The molds were capped and placed into an environmental chamber.

The specimens were cured at 79 ± 2°C for a total of 90 -0/+8 hours. The temperature corresponds to a measured peak for a 33% TDS cement-waste drum fitted with a thermocouple along the centerline. Total time includes the time needed for the drum centerline to cool to 30°C. Following the high-temperature cure, the cylinders were cured for a total time of 49 days.

After removal from the molds, the specimens along with the special instrumented specimen were inserted into the environmental chamber. Thirty temperature cycles were completed from 60°C to 20°C to -40°C and back with one hour soak periods at each temperature.

After removal from the chamber, the specimens were viewed. No spalling or cracking was noted. Average compression strength values of the cycled specimens was 1229 psi versus 1284 psi for specimens that did not undergo thermal cycling.

These positive results at the higher salt loading (33% TDS sludge wash solution) are suggestive of similar success at the lower salt loading (20% TDS sludge wash solution). WVNS will perform thermal cycle testing of cores taken from cement-waste drums made with sludge wash solution at the lower TDS loading. Results will be reported at a later date.

6.7 Free Liquids

Criteria: Waste specimens shall have less than 0.5% (by volume) of the waste as free liquids as measured by the method in Appendix 2 of ANS 55.1.

Waste Form: WVNS proposes alternate testing to meet this criteria. A three step approach is presented to show equivalence.

As noted in section 6.4, prior research was conducted with surrogate sludge wash solutions at 33% TDS. Step one was to prepare small-scale specimens (2" x 2" x 2" cubes) in the laboratory from non-radioactive sludge wash surrogate solution. Twenty-eight different cubes were prepared in a statistically-designed screening test (Plackett-Burman structure). Thirteen possible variables were used in the screening test as noted in Table 8.

Table 8
Twenty-Eight-Run Plackett-Burman Screening Test
Index of Variables

Variable	Number	Low	High
Sulfate	1	0.5x	2x
Nitrate:Nitrite Ratio	2	0.5	2.8
Organics	3	0.5x	4x
Aluminum (gm Al/gm Cl)	4	0	2.5
Total Solids (TDS)	5	25	37
Water:Cement Ratio	6	0.3	0.8
Calcium Nitrate	7	0.5x	2x
pH	8	11	13
Mix Time (mins)	9	4	16
Anti-foam	10	0.3x	2x
Sodium Silicate	11	0.5x	2x
Phosphate (gm PO_4/gm Cl)	12	0.01	7.0
Boron (gm B/gm Cl)	13	0.001	0.15

Note: Above values, when listed with an accompanying "x" are multipliers to the nominal 33% TDS sludge wash cement-waste formula presented in WVNS-TP-028A

Over the range of wt% TDS from 25 to 37, only the water-to-cement ratio was found to be statistically important in affecting gel time and 7-day cured compressive strength. Free water was present after 1 hour on only three cubes, which all had high water-to-cement ratios (0.80) and high trace phosphate levels (200% increase over lab-generated sludge wash solution). No free water was present after 24 hours.

Step two of the approach was to fabricate full-size drums using the 20% TDS surrogate sludge wash recipe. After curing, the drums were extensively cored. Almost 5% of the drum contents was sampled from side-to-side and top-to-bottom. No free liquids were detected. The cores provided material for baseline compressive strength tests, homogeneity verification, and immersion tests.

The final step to show equivalency is to perform a limited variability test on full-scale drums using actual radioactive sludge wash solution. WVNS will vary the water-to-cement ratio and TDS of the sludge wash solution. After curing, the drums will be cored and the absence of any free liquids established. Results of this test will be reported at a later date.

6.8 Full-Scale Specimen Test Results

Criteria: If small, simulated laboratory-size specimens are used to support the above tests, test data from cores of the full-scale products also should be obtained. Correlations between the performance of the lab-size specimens and the core data shall be prepared.

Samples shall be taken from throughout the entire full-scale waste form to ensure that product is homogeneous and all regions of the product will have compressive strengths of at least 500 psi.

Waste Form: For every key supporting test, cores from cement-waste drums have been the specimens of choice. Tests identified for future reporting shall be completed on core specimens. Verification specimens using cubes are discussed in section 6.10.2.

A cement-waste drum prepared with 20% TDS surrogate sludge wash solution had 18 cores (2 5/8" diameter x 5 1/4" length) removed. The cores were taken from different heights and distances to the centerline. The twelve cores tested to be statistically all from the same population and visibly showed no inhomogeneities. Six additional cores that underwent immersion testing also showed no inhomogeneities (see section 6.5). The proposed waste form is homogeneous and meets the 500 psi strength value for all regions.

6.9 Qualification Test Specimen Preparation

Criteria: Appendix A of the TP recommends certain precautions be taken during the mixing, curing, and storage of qualification test specimens. The goal is to produce specimens in the laboratory that are representative of the actual waste form product.

Waste Form: Two preliminary tests used laboratory specimens with a 33% TDS surrogate recipe to simulate the proposed waste form: thermal cycling and leachability. WVNS followed the recommendations in the TP to simulate the degree of mixing, method of curing, and storage of specimens before testing. As noted in section 6.8, these tests will be repeated on cores taken from drums filled with actual radioactive sludge wash solution.

6.10 Process Control Program

A Process Control Program shall be instituted to control the variables that influence the process and affect the final waste-form product. Previously for the WVDP supernatant cement-waste, a Process Control Plan (WVNS-PCP-001) was issued. A new version of the Process Control Plan (WVNS-PCP-002) is attached in the Appendix. This section discusses the key criteria cited in the TP and the features of the WVNS PCP that meet those needs.

6.10.1 Process Parameters

Criteria: The PCP shall identify and restrict within acceptable bounds variables that influence the process and affect the product.

Waste Form: As noted in section 6.7, screening tests were performed on a wide range of process variables. The only key variable for gel time and compressive strength was the water-to-cement ratio.

Only at excessive water-to-cement ratios (0.80) and excessive phosphate levels (200% increase over lab-generated sludge wash solution) was any free water detectable beyond 1 hour. After 24 hours no free water was detecable.

In addition, a variability test will be performed by WVNS to determine the key variables for success in the immersion test (see section 6.5). Samples with 33% TDS surrogate sludge wash solution failed the immersion test whereas those with 20% TDS surrogate sludge wash solution passed the test. In the latter case, the sulfate in the surrogate sludge wash solution was 40% higher than the actual sludge wash solution.

WVNS proposes three controls be set up to regulate the process:

- water-to-cement ratio
- TDS of sludge wash solution
- SO4 level

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WVNS proposes three controls be set up to regulate the process:

- water-to-cement ratio
- TDS of sludge wash solution
- SO4 level

WVNS proposes to produce the cement waste form at a water-to-cement ratio of 0.66 ± 0.02. Combined with this, the salt content of the LLW stream shall be controlled to 20 ± 1 wt% total solids. Along with a check on the level of sulfate, these controls regulate the relative proportion of sulfate-to-cement in the product (immersion performance).

These controls are the main variables that influence the process and the cement-waste product. All other variables fall within the wide operating ranges evaluated in the screening tests.

The order of addition is:

1) LLW solution
2) Antifoam
3) Cement blend
4) Sodium silicate solution

More specific information can be found in the Process Control Plan.

A wider range of water-to-cement ratios will be identified in the future variability tests noted above. When completed, the results of these tests will be reported along with the new control range for the CSS process.

6.10.2 Verification and Surveillance Specimens

Criteria: Prior to solidifying full-scale waste forms, verification specimens should be prepared for examination and compressive strength testing. The specimens should be free of significant visible defects (e.g. cracking or spalling) and should exhibit less than 0.5% by volume free liquid.

Compressive strengths should be measured within 24 hours after preparation. The values should be within two standard deviations of

0.14 gram SO4 per gram total salts. This limit corresponds to the level in the surrogate solution that passed immersion testing.

When the results of the immersion variability tests are in, new operating ranges will be defined for the full-scale CSS process. Results from these tests and an updated Process Control Plan will be provided at a later date.

Preparation of additional specimens for long-term performance testing is not required of the WVNS waste-form. The waste stream that is being solidified does not belong to the cited special class of waste streams (bead resins, chelates, filter sludges, and floor drain wastes) that require this effort.

7.0 CONCLUSIONS

This section summarizes the key qualification test results, and consolidates future testing commitments by WVNS for the proposed waste form.

7.1 Key Qualification Tests

Compressive strength of cores taken from cured full-scale product drums made with 20% TDS surrogate sludge wash solution yielded 1247 psi for an average of 12 samples. Immersion testing in both demineralized water and synthetic sea water showed excellent long-term physical stability. In demineralized water the average of three cores was 1722 psi; for sea water it was 1189 psi.

An alternate testing methodology is proposed to meet the specified free liquids limit. Laboratory tests with surrogate solutions between 25% and 37% TDS showed that only the water-to-cement ratio was key to compressive strength and gel time. The test also indicated only high water-to-cement ratios (0.80) and high phosphate (200% increase above lab-generated sludge wash solution) yielded any free water after 1 hour on small specimens. No free water was detected after 24 hours. Extensive coring of a full-scale drum filled with the 20% TDS surrogate sludge wash cement-waste has shown no free water. A final series of full-scale waste forms made with actual radioactive sludge wash solution with varying water-to-cement ratios and TDS levels will be produced and cored.

Tests with the same surrogate sludge wash solution at a higher salt content (33% TDS versus 20% for the proposed waste form) have shown success for leachability and thermal cycling. Radiation resistance and biodegradation tests of the waste form are not required.

7.2 Additional Waste Characterization Information

WVNS has produced nearly complete characterization information on the sludge wash solution that will be stabilized. Final updates to the characterization information will be provided.

7.3 Additional Qualification Testing

The proposed waste form meets and exceeds the various criteria set forth in the Technical Position paper. A few follow-up tests have been noted. These include:

1) Cores taken from actual radioactive 20% TDS sludge wash cement-waste drums will undergo thermal cycling and compressive strength testing.

2) Cores taken from actual radioactive 20% TDS sludge wash cement-waste drums will undergo leachability testing.

3) Cores taken from actual radioactive 20% TDS sludge wash cement-waste drums will undergo TCLP testing.

4) Free liquid determinations will be made on a series of actual radioactive 20% TDS sludge wash cement-waste drums produced at varying water-to-cement ratios and wt% TDS levels.

7.4 PCP Information

Tests in the laboratory have shown that very few controls are needed to produce a qualified waste-form. Key control variables for production of full-scale drums are:

- water-to-cement ratio:	0.66 ± 0.02
- salt in LLW stream:	20 ± 1 wt%
- sulfate in LLW stream:	< 14% of total salt.

Pending results of the immersion variability tests, WVNS will resubmit this report with the wider operating ranges.

During actual radioactive processing, verification samples will be taken from the tank feeding the full-scale solidification system. After preparation of a cube in the laboratory, visual confirmation of no free water and no physical degradation will be performed. A compressive strength measurement of the cube will be made and compared to a minimum value.

WVNS will prepare a series of cement cubes in the laboratory using actual radioactive sludge wash solution. The cubes will be made to the same specification as the full-scale process. A minimum 24-hour compressive strength value will be established using these specimens.

8.0 REFERENCES

1 "Technical Position on Waste Form", Revision 1, Technical Branch of the Low Level Waste Management and Decommissioning Division of the US Nuclear Regulatory Commission, dated January, 1991.

2 McVay, C. W, Stimmel, J. R, and Marchetti S., "Cement Waste Form Qualification Report - WVDP PUREX Decontaminated Supernatant", DOE/NE/44139-49 (DE89009019), August, 1988.

3 Rykken, Larry E., "High-Level Waste Characterization at West Valley: Report of Work Performed 1982 - 1985", DOE/NE/44139-14 (DE87005887), June 2, 1986.

4 Mahoney, John L., "Sludge Wash Cement Waste Form Qualification Development of Process Control Parameters:, WVNS-TSR-028, Revision 0, dated February 6, 1992.

5 Mahoney, John L., "Test Summary Results Report for Qualification Work for the Nominal Recipe for Cement Solidification of Sludge Wash Liquids", WVNS-TSR-026, Revision 0, dated February 6, 1992.

APPENDIX

WVNS-PCP-002 Process Control Plan for Cement-Waste with Sludge Wash Liquids