West Valley Demonstration Project

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TEST PROCEDURE

WATER TO CEMENT RATIO VARIANCE IN SIMULATED SLUDGE WASH

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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.

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 SHEET)

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-028 and WVNS-TPL-70-011. The objective of this overall testing criteria 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 [illegible]290 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 Sol.dification 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.

TEST SUMMARY REPORT

REV. 0

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 4/25/91

Engineering Release #2149

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.

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 per the analyses listed in Table 1.

Task Accomplished

This task remains open, pending the re-start of the Analytical & Process Chemistry ICP-AES instrument for radioactive samples. 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).

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:

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

4.1 Analyze Concentrates (objective 2.11)

Analyze the concentrates used in the preparation of a cement cube per the analyses listed in Table 1.

Action: Analytical & Process Chemistry
Timing: July 22, 1991

4.2 Revise the Test Summary Report

Update the TSR to reflect results from ICP and IC analyses of the concentrates used in the preparation of a cement cube.

Action: IRTS Engineering
Timing: August 15, 1991

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

G. A. Smith — J. C. Cwynar — L. E. ~~Michnik~~

D. C. Meess — Quality Assurance 7/23/91

TABLE 1
Requested Analyses for
Laboratory-Produced LWTS Concentrates

NO_2^-	K^+	PO_4^{-3}	Ti
NO_3^-	Na^+	SO_4^{-2}	Ca^{+2}
B	Cr		
Cl^-	Al	U	

pH	Total Dissolved Solids (TDS)
density	Total Suspended Solids (TSS)

alpha Pu	Cs-137	Sr-90	Tc-99
gross alpha	gross beta		

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
$Na_2MoO_4 \cdot 2H_2O$	0.051
$Na_2B_4O_7 \cdot 10H_2O$	0.091
Citric Acid ($\cdot 1H_2O$)	0.082
Oxalic Acid ($\cdot 2H_2O$)	0.082
Tartaric Acid (anhydr)	0.082
Na_2CrO_4	0.39
NaOH	1.11