ENCLOSURE 1

ATTACHMENT A

# WASTE FORM INTERIM QUALIFICATION REPORT
# WVDP STABILIZED SLUDGE WASH CEMENT-WASTE

Revision 1


Prepared By

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Waste Form Interim Qualification Report
WVDP Stabilized Sludge Wash Cement-Waste

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## 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 cementitious 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.

The next pretreatment step is being implemented at the WVDP. The HLW in Tank 8D-2 has been mobilized by five pumps, which allowed 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

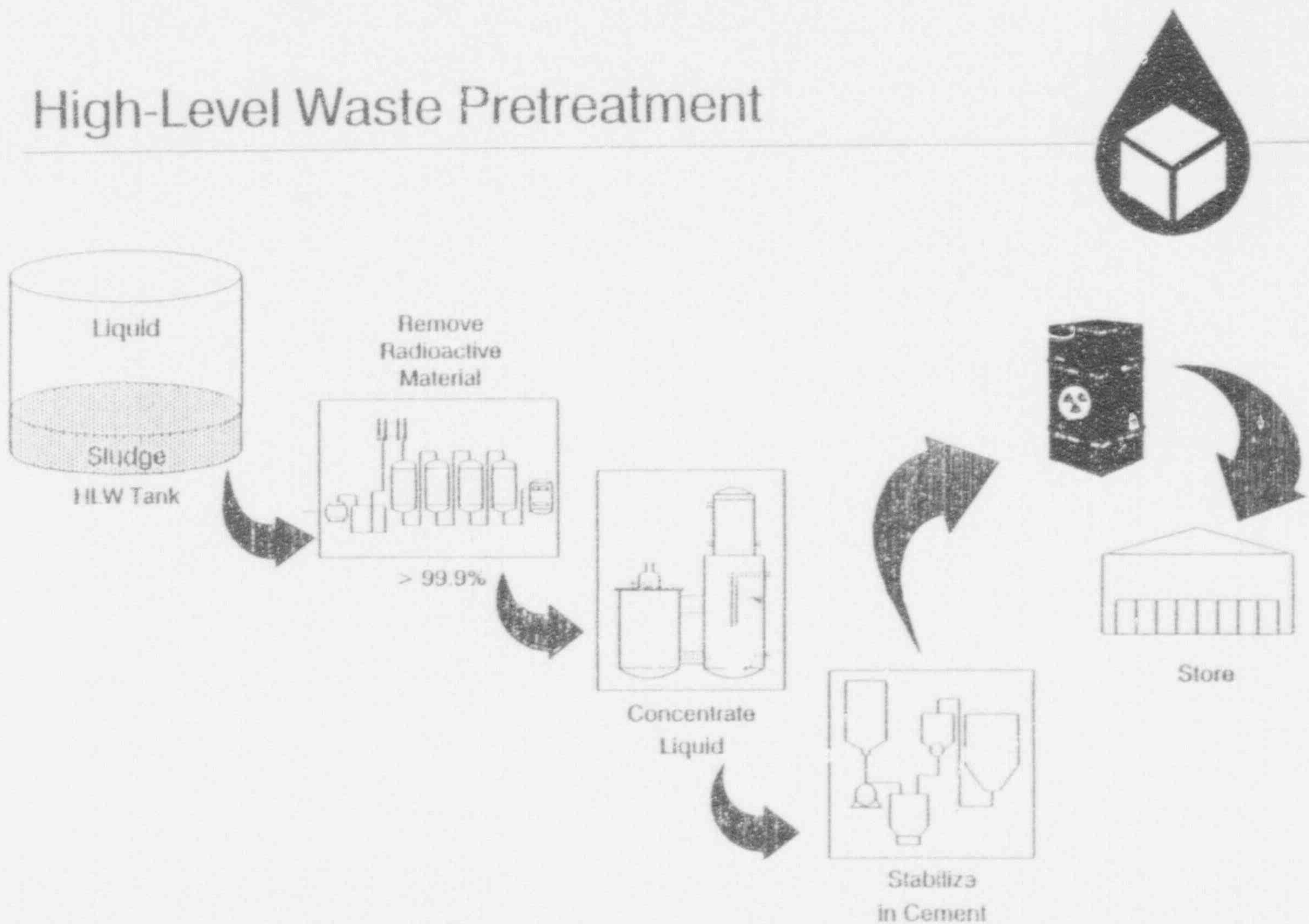



Figure 1

The resulting sludge wash solution will be treated in the ion exchange process as was done with the previous supernatant solution. A new 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 cementitious 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 waste loading in the sludge wash cement-waste material (compared to decontaminated supernate).

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. These new cement-waste forms will be stored with and may be disposed in conjunction with the previous decontaminated supernatant Class C cement-waste material, if the Environmental Impact Statement (EIS) for WVDP completion and site closure determines this is a desired option.

## 3.0 WASTE CHARACTERIZATION

The LLW stream for which data are presented to demonstrate qualification is decontaminated 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 solution compositions are shown in Table 1.<br><br>Non-radioactive surrogate solution used for qualification testing is shown in Table 2. |

Table 1

Chemical Composition of
Laboratory-Generated Sludge Wash Solution
& Preliminary Actual Sludge Wash Solution from Tank 8D-2

| | 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 |
| OH (est.) | 0.74 | 1.8 | 1.5 | 3.6 |
| pH | 12.2 | | 12.5 | |

* not used in surrogate solution

Note: Preliminary Tank 8D-2 analyses from sample #52 dated January 18, 1992. One 48-hour mixing campaign was performed on the sludge in Tank 8D-2 after this sample was taken. Analytical results on a few species indicate no significant change in composition.

## Table 2

### Chemical Composition of Surrogate Sludge Wash Solution For Cement-Waste Qualification Tests

| | Dry Wt% | g/l @20% TDS |
|---|---|---|
| Major: | | |
| Na | 31 | 73 |
| $NO_3$ | 27 | 62 |
| $NO_2$ | 22 | 51 |
| $SO_4$ | 14 | 33 |
| $CO_3$ | 2.6 | 5.9 |
| Minor: | | |
| K | 0.85 | 2.0 |
| Cl | 0.21 | 0.49 |
| Cr | 0.15 | 0.35 |
| P | 0.057 | 0.13 |
| TOC | 0.042 | 0.0[illegible]7 |
| Mo | 0.024 | 0.056 |
| B | 0.0037 | 0.0087 |

TOC = Total Organic Carbon

Note: Ca, Fe, U, and species in Table 3 not used in surrogate solution

## 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 |
| Ce | 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 actual 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 low-level radioactive 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 1[illegible] 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 cementitious 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* | 0.28 | 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 | --- | 0.0054 |
| 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 | --- | 0.043 |
| 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]

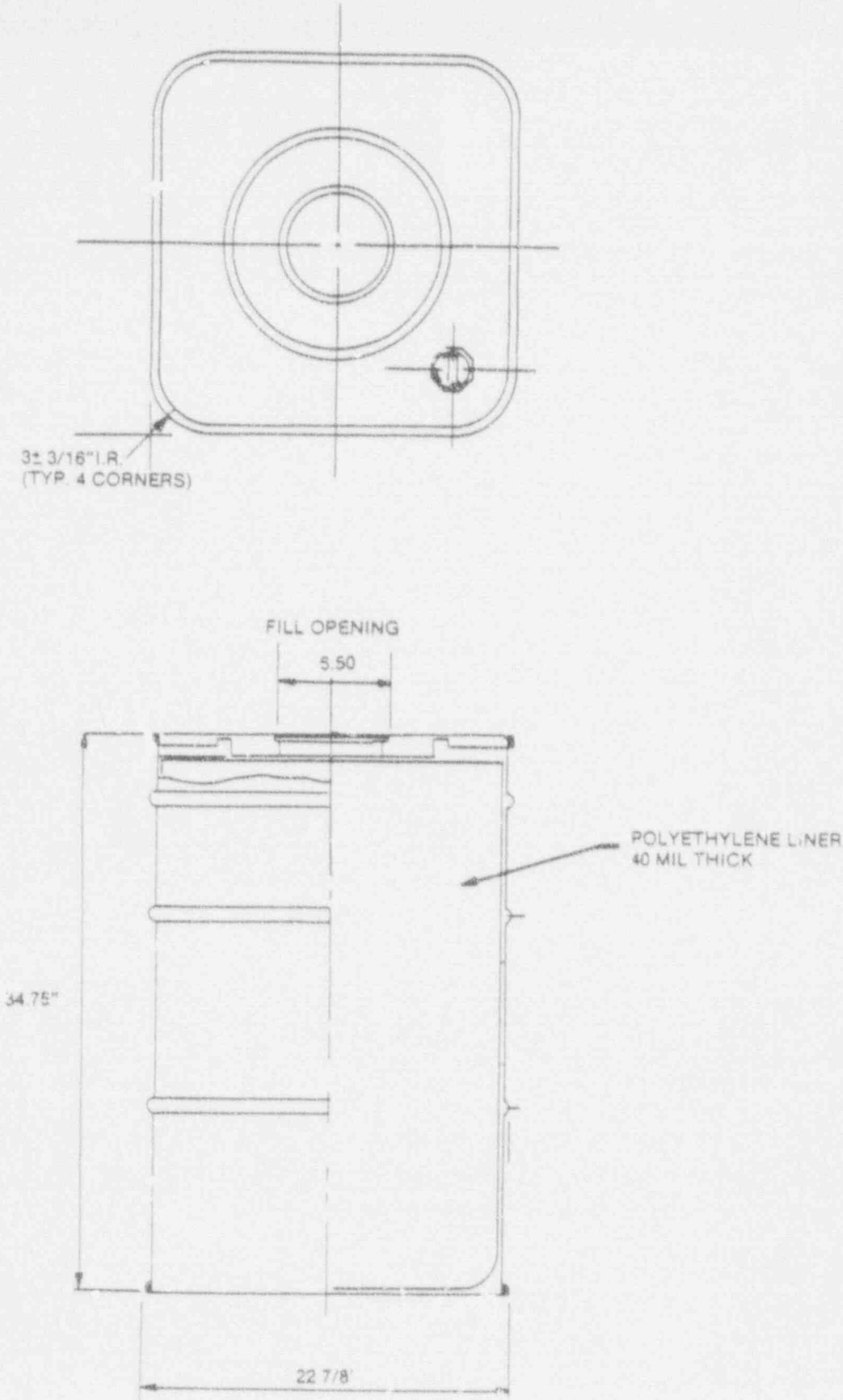

3± 3/16"I.R.
(TYP. 4 CORNERS)
FILL OPENING
5.50
POLYETHYLENE LINER
40 MIL THICK
34.75"
22 7/8"

Figure 2

## 4.3 Free Liquid

Criteria: Free standing liquid in the solid waste shall not exceed 1% of the solid volume.

Waste Form: Cement-waste product made with surrogate sludge wash solution has demonstrated no free liquid within one hour after creation of the cementitious material.

## 4.4 Reactivity of Product

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 Gas Generation

Criteria: The waste must not contain or be capable of generating toxic gases, vapors, or fumes harmful to persons tranrporting, 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 Pyrophoricity

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 Gaseous Waste

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. Previous supernatant cement-waste contained a comparable level of chromium. TCLP tests showed the cement matrix retained the chromium and was classified non-hazardous. A similar response is expected for sludge wash cement-waste. Other species considered hazardous per 40 CFR 261.24 are expected to be greatly below regulatory limits.

Results of TCLP testing of actual decontaminated 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 criterion in this section of the regulations specifies that void spaces within the waste and between the waste and its package must be reduced to the extent practicable. The steel drums that will contain the 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 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 a cement-waste drum prepared with non-radioactive 20 wt% TDS surrogate sludge wash solution following the 28-day minimum cure time. Results are shown in Table 6 and 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 38 days of curing. The average of all the cores is 1247 psi, well in excess of the 500 psi minimum.

## 6.2 Radiation Resistance

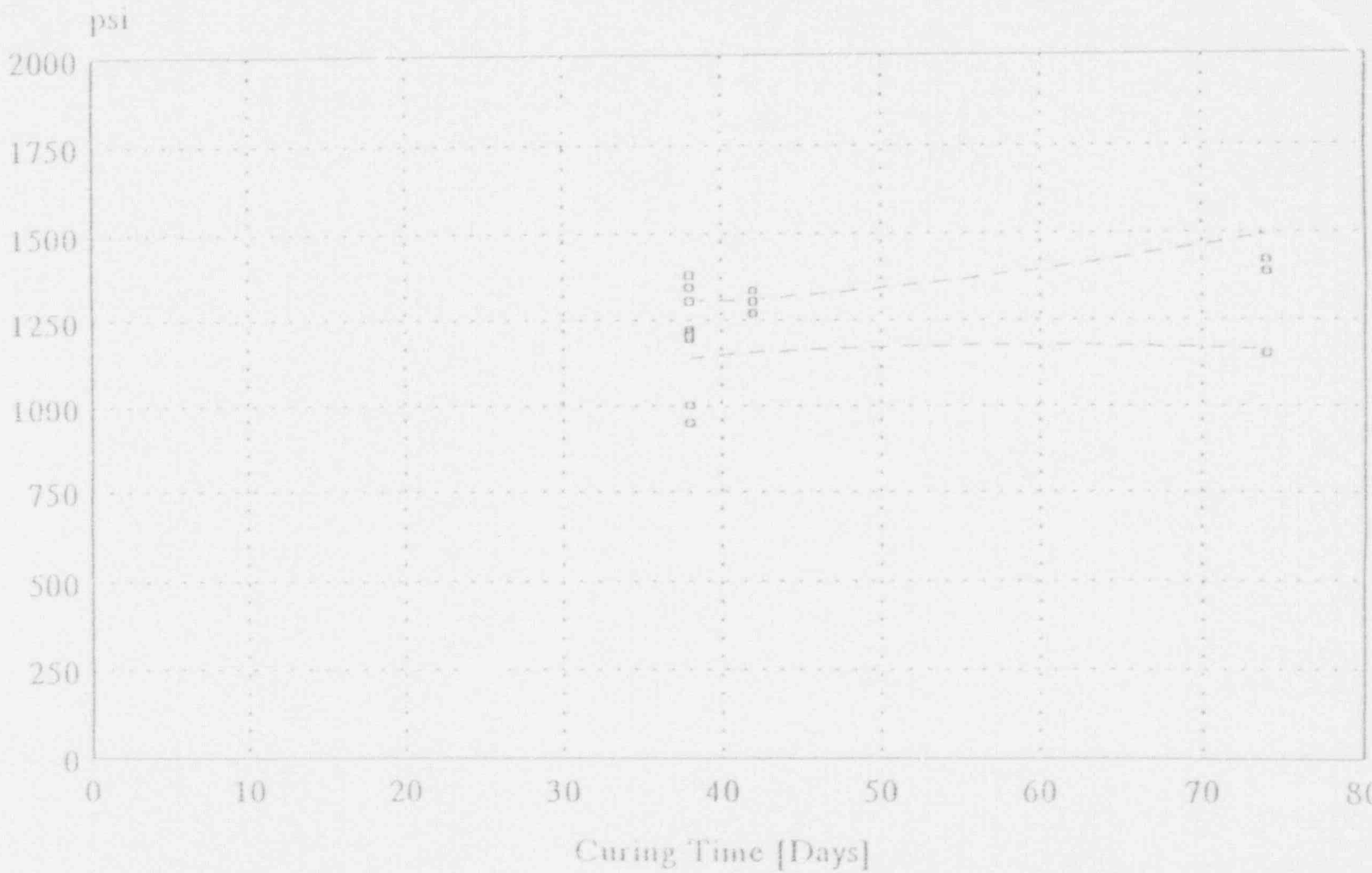
Waste forms containing ion-exchange resins or other organic materials shall be tested for radiation stability. The proposed WVNS waste form does not contain any ion-exchange resin and only trace quantities of organic materials, thus this test is not required.

Table 6

Compressive Strength Testing Results
Cores from 20% TDS Surrogate Cement-Waste Drums

| Cured Time Days | Compressive Strength psi |
|---|---|
| 38 | 951 |
| 38 | 1347 |
| 38 | 1002 |
| 38 | 1305 |
| 38 | 1221 |
| 38 | 1196 |
| 38 | 1213 |
| 38 | 1204 |
| 38 | 1381 |
| 42 | 1271 |
| 42 | 1305 |
| 42 | 13[illegible] |
| 74 | 1[illegible] |
| 74 | 138[illegible] |
| 74 | 1423 |
| Average | 1247 |

## Cured Cement Strength vs Curing Days
### Cores from Drums made with 20 wt% Surrogate Solution




Average = 1247 ± 76 psi (95% confidence of mean)

## 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.

## 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.

Decontaminated 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 7 and 8 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 decontaminated sludge wash solution at the lower TDS loading. Results will be reported at a later date.

## Table 7

### 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 | 12.962 |
| 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 | 7.885 | 10.424 | 7.9[illegible]7 | 11.751 |
| 7 | 8.010 | 10.726 | 8.289 | 11.924 |
| 24 | 7.797 | 11.392 | 8.060 | 13.235 |
| 48 | 8.026 | 10.850 | 8.393 | 11[illegible] |
| 72 | 8.459 | 10.637 | 8.847 | 11[illegible] |
| 96 | 8.879 | 11.509 | 9.225 | 11.[illegible] |
| 120 | 9.138 | 11.783 | 9.598 | 12.1[illegible] |

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 8

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

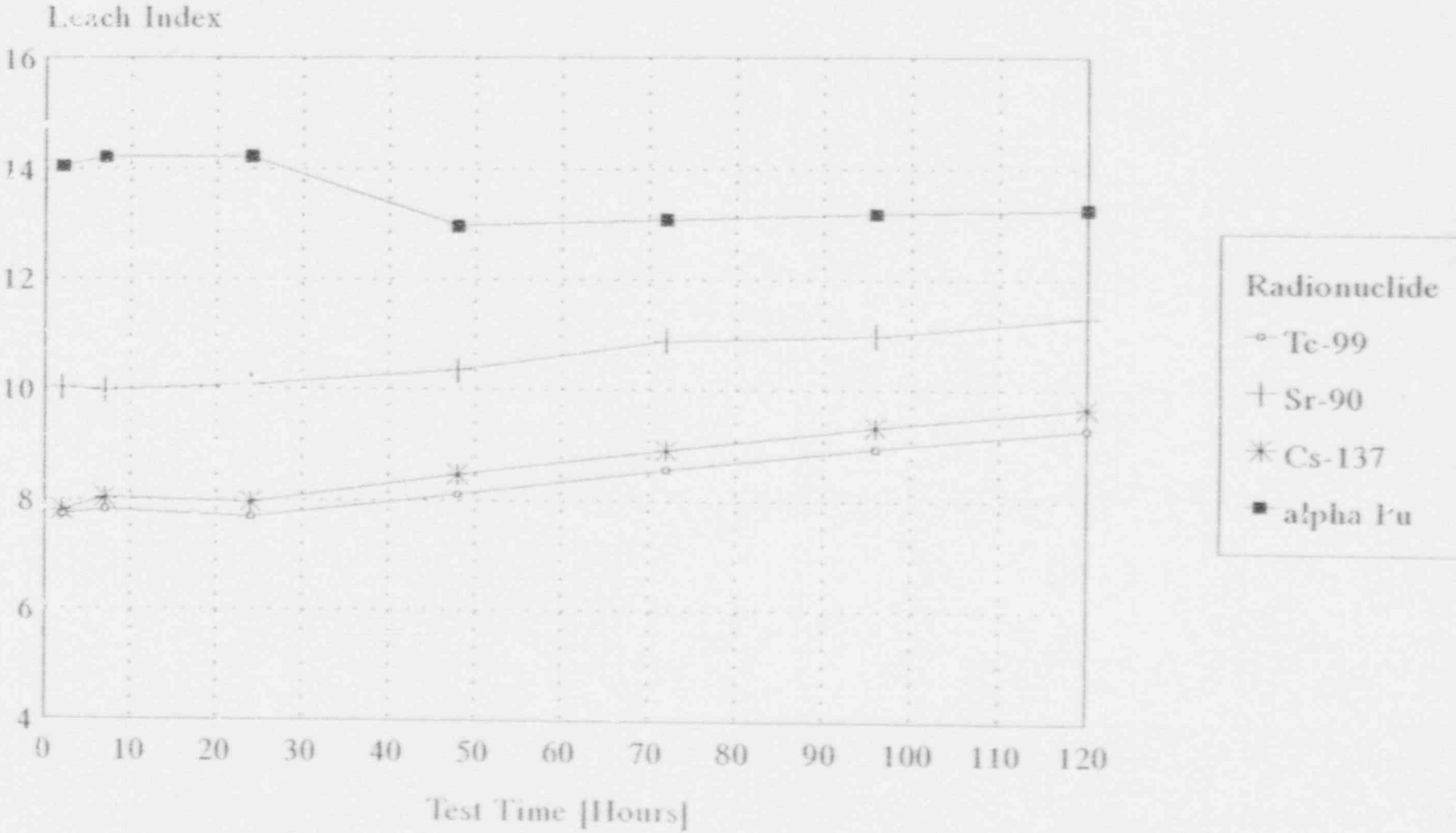
Delta = difference between averages

Signif Level = 95% confidence value for differences between the two averages

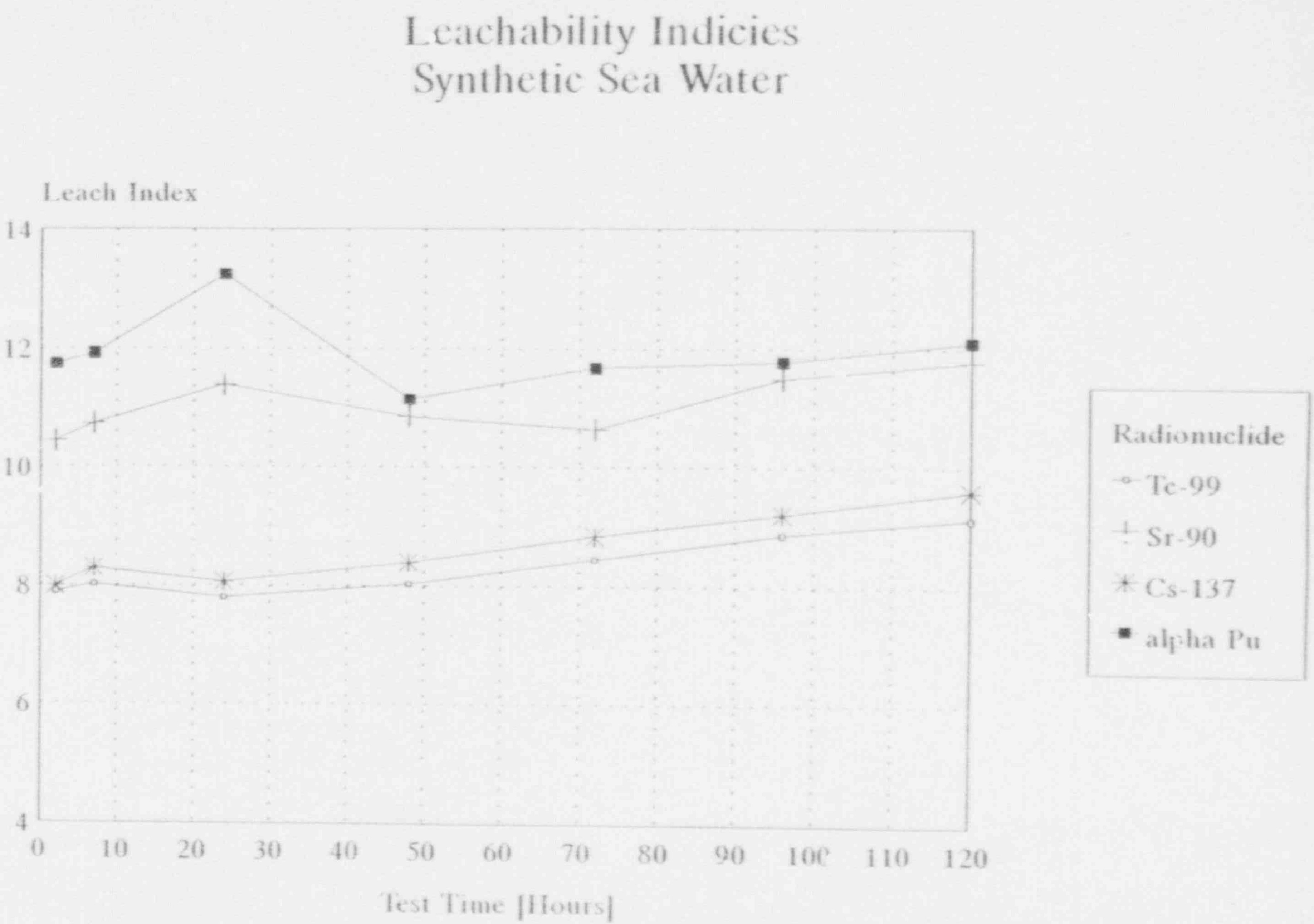
Diff = Is delta more than the significance level?

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




Simulated Cement-Waste from 33% TDS solution

## 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 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 a full-scale cement-waste drum prepared with non-radioactive surrogate sludge wash solution at 20 wt% TDS. Three cores were placed into demineralized water and three into synthetic sea water.

After 90 days of immersion, the specimens showed only minor cracking (photographs attached in the Appendix). Compression testing after immersion in demineralized water yielded 2163, 1145, and 1860 psi for an average strength of 1722 psi. For synthetic sea water the values were 1212, 1178, and 1178 psi for an average of 1189 psi.

Compared to the un-immersed baseline average of 1247 psi these represent an increase of over 30% and a decrease of under 5% respectively. Based on these results, the proposed waste form made with 20 wt% TDS sludge wash solution meets the 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 and water-to-cement ratio. 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.

Three 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 at ambient temperature 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. Compression results for the cycled cylinders were 1079, 1324, and 1283 psi for an average strength of 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.

Table 9
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

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 9.

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 produce a full-size drum using the 20% TDS surrogate sludge wash recipe. After curing, the drum was extensively cored. About 5% of the drum contents were 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 decontaminated 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 more than 21 cores (2 5/8" diameter x 5 1/4" length) removed. The cores were taken from different heights and distances to the centerline. Compression results of 15 cores tested to be statistically 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) has been prepared and is listed as reference 6. This section discusses the key criteria cited in the TP and the sections of the WVNS PCP that meet those criteria.

#### 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 detectable.

In addition, a variability test will be performed 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 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
- $SO_4$ 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 to ensure that the sulfate concentration is below the maximum limit, 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 generate acceptable product as long as the parameters fall within the 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 the mean value generated during waste qualification testing.

For certain waste streams (bead resins, chelates, filter sludges, and floor drain wastes) additional specimens are to be prepared for long-term performance testing.

Waste Form: As noted in the Process Control Plan, samples of the decontaminated sludge wash solution are sent to the laboratory for preparation of cube verification specimens. After curing for 24 hours, the specimens are viewed for defects and any free water, then the cubes tested for compressive strength.

WVNS will complete a series of cement cubes in the laboratory using actual sludge wash solution. The cubes will be made to the same specification as the full-scale process:

- -water:cement ratio 0.66 ± 0.02

- -TDS of solution 20 ± 1 wt%

A minimum 24-hour compressive strength value will be established using these specimens.

This verification step will show that the waste stream can be prepared into a dry cement-waste form with good compressive strength.

As noted in section 6.5, a variability test will be performed by WVNS to determine the acceptable range for water-to-cement ratio and wt% TDS. Lacking this data, WVNS has chosen to restrict the process to a very tight water-to-cement ratio and wt% solids in the sludge wash solution. Test specimens in this range have successfully passed the 90-day immersion test.

In addition, the sulfate in the LLW stream will be measured and verified against an upper limit of 0.14 gram $SO_4$ 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 available, 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 a cured full-scale product drum made with 20% TDS surrogate sludge wash solution yielded 1247 psi for an average of 15 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 decontaminated 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 (Tables 1, 4 and 5) 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 decontaminated sludge wash cement-waste drums (at 24% TDS) will undergo thermal cycling and compressive strength testing.

2) Cores taken from actual decontaminated sludge wash cement-waste drums (at 24% TDS) will undergo leachability testing.

3) Cores taken from actual decontaminated sludge wash cement-waste drums (at 24% TDS) will undergo TCLP testing.

4) Cores taken from actual decontaminated sludge wash cement-waste drums will undergo immersion testing in synthetic sea water. A series of drums ranging from 20% TDS to 27% TDS, and from 0.62 to 0.70 water-to-cement ratio will be produced and tested.

5) Free liquid determinations will be made on a series of actual decontaminated sludge wash cement-waste drums produced at the wt% TDS and water-to-cement ratios noted above.

## 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 salts |

Pending results of the immersion variability tests, WVNS will resubmit this report with the wider operating ranges.

During actual radioactive sludge wash 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 decontaminated 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.

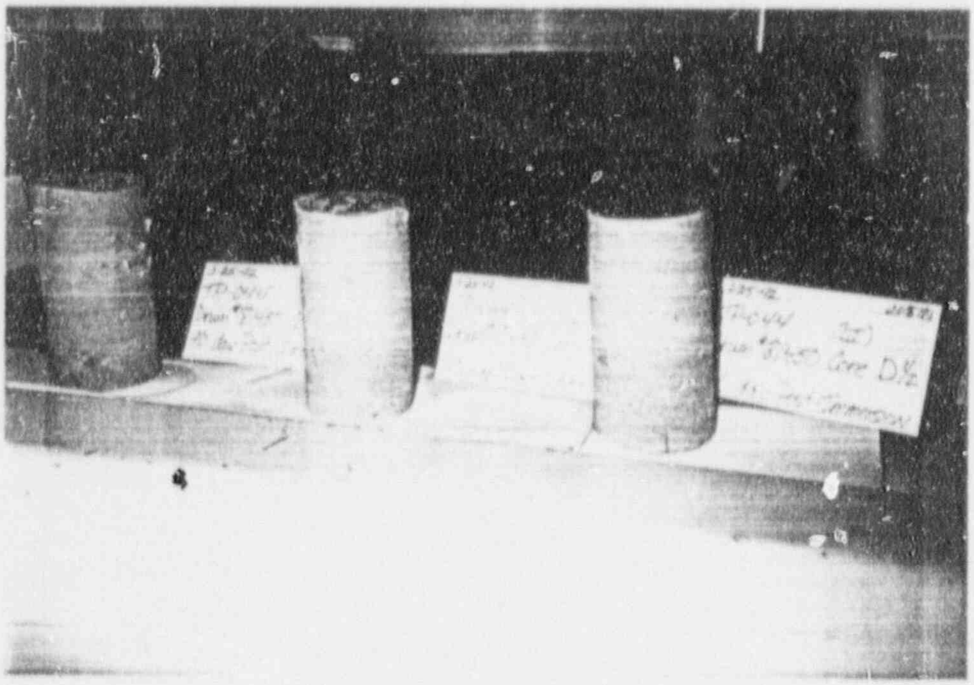
4 Mahoney, John L., "Sludge Wash Cement Waste Form Qualification Development of Process Control Parameters:, WVNS-TSR-028, Revision 0, dated February 6, 1992.

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.

6 "Process Control Plan for Cement Solidification of Sludge Wash Liquid", WVNS-PCP-002, Revisicn 0, dated May 19, 1992.

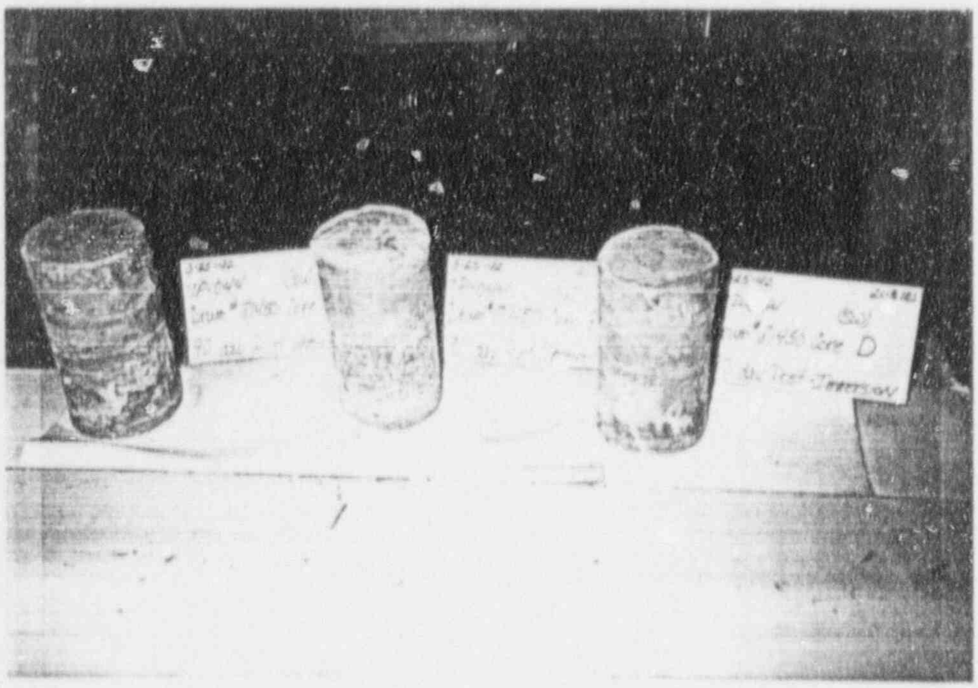
# APPENDIX

PHOTOGRAPHS OF IMMERSED CORES



CEMENT CORES FOLLOWING 90-DAY IMMERSION TEST
IN DEMINERALIZED WATER

NOTE: CORES OBTAINED FROM DRUMS PRODUCED FULL SCALE IN CSS WITH 20% TDS NONRADIOACTIVE SURROGATE SLUDGE WASH SOLUTION



CEMENT CORES FOLLOWING 90-DAY IMMERSION TEST
IN SYNTHETIC SEA WATER

NOTE: CORES OBTAINED FROM DRUMS PRODUCED FULL SCALE IN CSS WITH 20% TDS NONRADIOACTIVE SURROGATE SLUDGE WASH SOLUTION

ENCLOSURE 2

ATTACHMENT B

WVNS-PCP-002