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UNITED STATES
NUCLEAR REGULATORY COMMISSION
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March 21, 1995

MEMORANDUM TO: Gary C. Comfort, Jr.
Licensing Section 2
Licensing Branch
Division of Fuel Cycle Safety
and Safeguards, NMSS

FROM: Joseph Kane and Robert Lewis RL JDK
Engineering Section
Engineering and Geosciences Branch
Division of Waste Management, NMSS

THRU: Michael J. Bell, Chief M Bell
Engineering and Geosciences Branch
Division of Waste Management, NMSS

SUBJECT: TRANSMITTAL OF TECHNICAL EVALUATION REPORTS FOR "WASTE FORM QUALIFICATION PROGRAM FOR CEMENT SOLIDIFICATION OF SLUDGE WASH LIQUID," FOR STABILIZATION IN TYPE I OR TYPE V PORTLAND CEMENT (TAC NO. L21412)

The Division of Waste Management (DWM) has completed technical reviews of the subject waste form qualification programs submitted by the West Valley Project Office of the Department of Energy (DOE). Enclosure 1 is the Technical Evaluation Report (TER) for the Type I Portland cement recipe, and Enclosure 2 is the TER for the Type V recipe. Brookhaven National Laboratory (BNL) has provided technical assistance through contract in the development of the Type V recipe TER. BNL was also involved in the early stages (i.e., prior to the immersion failure of the transition drums) of the Type I recipe review, and results of those review efforts are incorporated into the Type I TER.

Both TERs present a positive determination as to the ability of the solidification technologies to produce waste forms which meet the stability provisions of 10 CFR 61.56 and the associated guidance in the Branch Technical Position on Waste Form, Rev. 1. Full concurrence with this determination is contingent upon continued positive results from the long-term test programs and resolution of minor issues which are identified in Section 5 of each TER.

Because of the similarities in the stabilization technologies, DWM suggests that both TERs be transmitted to DOE as two enclosures under one cover letter. In Enclosure 3, DWM has provided you an example cover letter, which addresses the conditions of approval and the continuing DOE actions. Upon request, we will e-mail a copy of the file for your Division to finalize. Please note that the letter forwards a copy of the TERs to the Office of State Programs and the State of New York. This action is typical for approved topical reports, but its applicability to the West Valley review is left for your judgment.

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In the future, DWM would like to continue to be involved in the review of results of the long-term tests as they are submitted by DOE. Questions or additional information concerning the Type I review can be directed to Robert Lewis on 415-6680, and that concerning the Type V review can be directed to Joseph Kane on 415-6667.

Enclosures: As stated

cc: B.Bowerman (BNL)
B. Siskind (BNL)

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Enclosure 1

TECHNICAL EVALUATION REPORT
WASTE FORM QUALIFICATION PROGRAM - VOLUME 2
CEMENT SOLIDIFICATION OF SLUDGE WASH LIQUID
WITH TYPE I PORTLAND CEMENT
WEST VALLEY DEMONSTRATION PROJECT

Prepared by the U.S. Nuclear Regulatory Commission
Office of Nuclear Material Safety and Safeguards
Division of Waste Management

March 1995

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1. INTRODUCTION

The United States Department of Energy (DOE) is conducting a cleanup of stored high-level radioactive waste at the Western New York Service Center in West Valley, New York. The West Valley Demonstration Project Act of 1980 (Public Law 96-368) established the project and requires the DOE to consult with the Nuclear Regulatory Commission (NRC) on these activities. Low-level radioactive wastes (LLW) produced by the project during the cleanup are being processed for ultimate disposal. DOE has been conferring with the NRC on a variety of aspects of the disposal of LLW at the Service Center.

The DOE has provided the NRC with the information and data on the cement solidification of the sludge wash liquids in a report entitled "Waste Form Qualification Program for Cement Solidification of Sludge Wash Liquid" (Ref. 1). Volumes 1 and 2 of this document describe efforts to qualify recipes used to stabilize the sludge wash with Type I Portland Cement as a solidification agent. Volume 1 describes a recipe which was abandoned due to problems encountered during qualification work, and Volume 3 discusses stabilization with Type V cement and is the subject of a separate NRC Technical Evaluation Report (TER)(Ref. 2). This NRC TER evaluates the cement-solidified sludge wash waste form, as described in Volume 2 of the Qualification Program, against the structural stability requirements for waste forms set forth in the Federal regulations in 10 CFR Part 61.

In May 1983, NRC provided guidance (Ref. 3) to waste generators and processors for meeting the stability requirements of 10 CFR Part 61 by issuing the Technical Position on Waste Form (TP). The TP stated that structural stability could be achieved by processing (or solidifying) the waste or by placing the waste in a container (e.g., a high integrity container) or structure. Since the issuance of the TP, NRC staff have provided additional guidance to address troublesome issues uncovered in solidification operations. As an example, cement is commonly used to stabilize LLW; however, field experience and laboratory testing indicated that unique interactions can occur between the cement constituents and some components present in the waste materials which degrade the stability of the product waste form. Because of these experiences, the structural stability of the portland-cement-based waste forms was the major topic of discussion at a workshop on the cement solidification of LLW (Ref. 4). Subsequently, NRC revised the TP in January 1991 (Ref. 5) to include Appendix A, dealing with qualification testing, performance confirmation, and reporting of mishaps for cement-based waste forms.

This TER prepared by NRC staff evaluates the documents submitted by West Valley Nuclear Services (WVNS), the contractor conducting the radioactive waste operations for DOE at the West Valley site. The purpose of this review is to determine whether or not the cement solidification of the sludge wash by the process described in these documents using Type I Portland cement meets the structural stability provisions of 10 CFR 61.56 and the relevant portions of the TP (Ref. 5), including Appendix A on LLW stabilization with cement. The next two sections provide a short history of LLW stabilization at West Valley and a brief description of the documents supplied by WVNS. Section 4 presents NRC evaluation as to whether the proposed test plans and procedures will assure the production of waste forms that meet the long-term structural stability criteria. Conclusions are summarized in Section 5. NRC's contractor, Brookhaven National Laboratory assisted in the technical review of the DOE documents and was a contributor to the findings in this TER.

2. BACKGROUND

The largest volume of liquid LLW processed at West Valley resulted from the treatment of the high-level waste liquids and sludge contained in Tank 8D-2. This supernatant was passed through zeolite beds to remove Cs-137, the major radionuclide contaminant, from the supernatant. The effluent from the zeolite beds, the so-called "decontaminated" supernatant, still contained some activity and was stabilized in cement.

Before the initial processing of decontaminated supernatant, WVNS developed a Portland I cement binder recipe using a simulant of the supernatant. Tests in the full-scale production facility yielded a product with entrained air, low density, and a lower-than-expected compressive strength. These problems were corrected by adding an antifoaming agent. Subsequent small scale tests with actual decontaminated supernatant indicated the presence of set retarders, probably organic chelating agents or their degradation products acting in conjunction with chromate ion. Calcium nitrate and sodium silicate additives counteracted the effects of the set retarders so that an acceptable waste form could be produced (Ref. 6).

With the supernatant processing completed, the next planned phase was the washing of the sludge now at the bottom of Tank 8D-2. This sludge consisted of a layer of solids composed of insoluble oxides, hydroxides and carbonates as well as sodium sulfate (Na_2SO_4). To wash the sludge layer, water was added to the tank and recirculated to dissolve the Na_2SO_4. Sulfate must be removed before the sludge layer can be vitrified, since sulfates would separate from the molten glass. During laboratory-scale testing of the sludge wash process, substantial quantities of plutonium and uranium compounds were released into solution, indicating the potential for producing transuranic waste rather than LLW. An alternative decontamination technique consisting of pH control of the sludge wash water in conjunction with use of a titanium-coated IE-96 ion exchange medium was used to remove the bulk of the cesium, plutonium, and strontium from the sludge wash (Ref. 7). The liquid collected from the wash was evaporated to reduce waste volumes, then solidified in cement.

This report details NRC review of the process for stabilization of the resulting decontaminated sludge wash using Portland Type I cement. WVNS has tested two recipes for processing sludge wash with Type I Portland cement. The first recipe involved a waste stream that left the evaporator at a nominal 32% total dissolved solids (TDS). This number was selected because it is near the physical limit for TDS in which the evaporator can operate without precipitating bulk sulfate solids. The resulting recipe did not perform satisfactorily when subjected to the 90 day immersion test identified by the TP. The reason for the failures was determined to be the higher sulfate concentration of the sludge wash waste, as compared to the supernatant waste stream which was solidified using a similar recipe.

Two alternate courses of action were selected by WVNS, including (1) lowering the TDS of the evaporated waste to 20 weight percent and keeping the remaining recipe constant (i.e., type I cement), or (2) changing to Portland Type V cement (i.e., sulfate resistant Portland cement) and keeping the remaining recipe constant (i.e., stay near 32 %TDS). Operating experience with the supernatant recipe was the basis for the decision to retain admixtures constant for both options. This TER deals with the first of the options. A nominal TDS of 20% for the Type I recipe was selected, in part, because it would produce a number of drums that would just fill the remaining storage capacity of the on-site drum storage cell.

3. SUMMARY OF REVIEWED DOCUMENTS

WVNS submitted a series of documents in a loose-leaf binder that comprises Volume 2 of Reference 1. Two of the documents from Volume 2, the Qualification Report and the Process Control Plan, are summarized below and were reviewed in detail. For other documents in the notebook, WVNS uses the designations: "Test Request (TRQ)," "Test Procedure (TP)," and "Test Summary Report, (TSR)" to describe, respectively, the planning, performance, and results of a particular testing series. Also, each testing protocol has associated with it a unique number (e.g., TRQ-051, TP-051, and TSR-051 would all reference the same test series). The test series documents provide specific details of how data were produced to support the Qualification Report and Process Control Plan. For this NRC TER, a term such as XXX-051 may be used when reference is made to a test series. The bulk of qualification work was performed under three test series, which are also summarized below.

The first major document reviewed was titled: **"Waste Form Qualification Report: WVDP Stabilized Sludge Wash Cement-Waste with Type I Portland Cement," Rev. 0, August 24, 1994, WVNS-TR-70-024. Prepared by W. J. Dalton.** This document will be herein referred to as the Qualification Report, or the QR. The QR summarizes the treatment of the sludge wash liquids, and their characteristics. The Qualification Report describes the recipes developed for stabilization in Portland Type I cement, and the tests conducted to show that the process will produce a stable waste form in accordance with 10 CFR Part 61 and Appendix A to Rev. 1 of the NRC Technical Position on Waste Form (Ref. 5). The Qualification Report, Rev. 1, was reviewed by NRC in 1993 and a request for additional information (RAI) (Ref. 8) was sent to WVNS under cover letter dated August 19, 1993. WVNS responded formally on November 16, 1993 (Ref. 9). The QR, Rev. 1 was reissued as Rev. 0, and submitted to NRC under cover letter dated September 8, 1994. This revision was made, in part, to incorporate commitments provided in the responses to the RAI. This TER includes consideration of information provided in both the revised QR and the responses to the RAI.

The second major document reviewed in detail was titled: **"Process Control Plan for Cement Solidification of Decontaminated Sludge Wash Liquid," Rev. No. 9, August 23, 1994, WVNS-PCP-002. Prepared by M. N. Baker.** The Process Control Plan (PCP) describes the processes, operating restrictions, and systems used to produce the stabilized sludge waste liquids. Specific details about waste composition limits and verification procedures for laboratory samples and final waste forms during production are also given. These are presented below in Section

4.4.10. Rev. 4 of the PCP was the document originally reviewed by NRC when staff produced the RAI. WVNS revised the PCP, producing Rev. 9, to incorporate revisions and commitments made in response to the August 19, 1993 RAI. This TER includes consideration of the revision.

The majority of qualification work involved three test series, although several supporting test series exist. Because the three primary test series will be frequently referenced herein, a summary of each is provided here.

"Waste Form Qualification Work for Sludge Wash Liquids" (XXX-044). This test series was initiated subsequent to the immersion test failure of the initial Type I sludge wash recipe, which was based on the supernatant recipe at about 33 wt% TDS. XXX-044 was performed to qualify two alternate recipes, using lower wt% TDS, that could perform satisfactorily during the immersion test. TDS was tested at 14 wt% and 20 wt%, and other ingredients and proportions were held constant from the previous recipe. Testing performed under XXX-044 utilized a surrogate sludge wash formula as opposed to actual waste. Cored specimens from full-scale waste drums were evaluated against the tests given in the TP. Additionally, cylinders cast from scoop-samples of full scale drums before setting were subjected to some of the TP tests.

"Sludge Wash Cement-Waste Windows of Composition" (XXX-051). The purpose of this testing program was to qualify the 20 wt% TDS alternate recipe that was developed during XXX-044 testing, using actual waste. Decontaminated sludge wash at a nominal 20 wt% TDS, but also at 24 and 27 wt% TDS, was solidified in Type I cement and admixtures to create seven drums. The drums were spiked with a sulfate solution to provide for an operating margin during production. The drums were cored after a minimum 28 days and evaluated against the tests given in the TP (with the exception of the leach test).

The qualification report also details results of additional qualification testing performed on cored samples from actual production drums. This additional testing was performed on drums from solidification **Campaign 22-1S**, and was necessitated by the failure in immersion of the XXX-051 cores (further discussed in section 4.4.5, below). Campaign 22-1S cores were subjected to testing as described in the TP, with the exception of the thermal cycle test.

4. TECHNICAL EVALUATION

The following technical evaluation compares information provided in the Qualification Report and Process Control Plan with the applicable regulatory requirements of 10 CFR Part 61 and the guidance in the 1991 Rev. 1 TP, Appendix A, on cement-solidified waste forms (Ref. 5).

In general, the qualification program developed by WVNS is more extensive than NRC guidance given by the TP. WVNS has tested both lab-scale specimens and cores from full-scale specimens using both simulated and actual waste. Additional work was performed on cores taken from actual production drums.

4.1 Characterization of Waste Composition

Appendix A to the January 1991 Rev. 1 TP describes waste characterization as including at least the following minimum information:

- identification of major constituents (e.g.,resin type, diatomaceous earth, crud) including primary ions/salts and other solids,
- density,
- pH,
- temperature,
- a check for the presence of secondary constituents that could significantly affect the hydration of the cement*, and
- radioisotopic analysis.

Characterization should include quantitative information on the major constituents, namely, anticipated ranges of concentrations or percentage compositions, and anticipated ranges of the density (or specific gravity), pH, and temperature. Also, a solidification process should demonstrate a correlation between the waste formulations used to prepare the qualification test specimens and the actual wastes encountered in the field in terms of the characteristics listed above (with the exception of the radioisotopic analysis, which is needed for waste classification purposes). Because a given type of waste stream will often differ in these characteristics from one nuclear power plant to another and over the course of time at any one power plant, it is impractical for waste processors in the commercial sector to perform qualification testing on every possible combination and concentration of minor constituents in that waste stream. Nor is it considered practical or necessary for a waste processor to perform a complete quantitative chemical analysis on every batch of waste that is produced. It is, however, necessary for waste generators and processors to be cognizant of the types of chemicals which may cause problems for cement solidification of radwaste so that contamination of the waste stream may be prevented, or the waste pre-treated, as appropriate, if the problem constituents are contained in the waste stream.

WVNS does not expect the sludge wash liquids to exhibit the degree of variation encountered in commercial nuclear power plant waste. This review primarily focussed on the chemical and physical characteristics of the sludge wash waste. The items evaluated are as follows:

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*NRC Information Notice 90-31[6] and Table I of Appendix A to Rev. 1 TP list most such secondary constituents, but not necessarily all of them.

Major constituents: The sludge wash at a nominal 20 wt% TDS is a solution composed primarily of nitrate, nitrite, and sulfate salts of sodium (about 92% of the total salts). The specific fractions, along with standard deviations, of each major constituent of the sludge in tank 8D-2 are presented in Table 1, below, and in Table 2 of the QR. The composition in terms of dry wt% does not change during the decontamination (ion exchange) process or evaporator operation. Samples taken monthly from Tank 8D-2 are analyzed for major constituents and properties (e.g., pH), and are used to verify that the composition of the waste does not significantly change. Because sulfate concentration has a significant impact on waste form performance, samples from each batch of concentrated, decontaminated sludge wash are analyzed for sulfates as part of the PCP. It is notable that the sludge wash waste is more homogenous in chemical composition than most commercial LLW.

The total for major and minor constituents in Table 2 of the QR account for about 93 wt% for the samples taken at the start of processing, and 96% for those taken during processing. The presence of other dissolved constituents or uncertainties in the values presented could account for the remainder of solids in the waste stream. The presence of unidentified minor constituents or deviations in the nominal compositions are of little concern unless they interfere with the solidification process.

Table 1
Major Constituents in Tank 8D-2 Sludge Wash #1

Constituent	At Start of Processing (wt% solids)	During Processing (wt% solids)
Sodium (Na^+)	30.47 $\pm$ 0.841	32.34 $\pm$ 2.52
Nitrate (NO_3^-)	27.76 $\pm$ 0.297	25.03 $\pm$ 2.20
Nitrite (NO_2^-)	24.43 $\pm$ 0.509	25.52 $\pm$ 1.81
Sulfate ($SO_4^=$)	10.21 $\pm$ 0.718	9.64 $\pm$ 0.91

Density: The density of the decontaminated sludge wash is given on Table 2 in the QR, and is sampled during processing pursuant to the PCP. The density was measured to be 1.155 $\pm$ 0.003 g/mL at 20 wt% TDS for 4 samples taken at the start of processing, and 1.131 $\pm$ 0.020 g/ml for 16 monthly samples taken during processing in the period from April 27, 1992, to May 5, 1994. The density varies directly with wt% TDS, from 1.154 g/ml at 19 wt% TDS to 1.166 g/ml at 21 wt% TDS.

pH: The pH of the concentrated decontaminated sludge washes is one of the variables controlled under the PCP and is limited to values higher than 12.0. Its value during qualification work was 12.0 to 12.6 during Campaign 22-1S, 12.0 during XXX-044, and 10.4 during XXX-051. The low pH of the XXX-051 drums is thought to have contributed to their immersion test failure (further discussed below in Section 4.4.5).

Temperature: The QR states that the temperature of the concentrated decontaminated sludge wash is ambient, which, for the cement solidification system is about 90°F.

Minor constituents: Minor organic constituents were discovered to cause cement set problems in the initial supernatant solidification campaign. In response to the RAI, WVNS revised Table 2 in the QR to report total organic carbon and total inorganic carbon as 0.0235 $\pm$ 0.00265 wt% total solids and 1.092 $\pm$ 0.230 wt% total solids, respectively. This verifies WVNS' claim that organics present are at concentrations less than 500 parts-per-million, for which clarification was requested in the RAI. WVNS also identified, in the response to the RAI, that any Tank 8D-2 additions are prohibited from containing organics.

Radionuclides: Because of the nature of the waste stream (i.e., LLW resulting from treatment of reprocessing liquids), there are several radioisotopes present in the waste. Quantities and proportions of isotopes can vary during processing depending on the efficiency of the ion-exchange process, which is a function of the remaining exchange capacity of the resins and zeolite media. Cs-137, Sr-90, and transuranic concentrations are most affected by this. Cs-137 concentration in the waste stream is monitored as a process control limit to control worker exposures during operations.

Tables 3 and 4 of the QR give radionuclide concentrations in the sludge wash. The highest concentrations of nuclei observed in the decontaminated sludge wash were 0.642 μCi/mL for Cs-137, 0.137 μCi/mL for Sr-90, and 4.04 nCi/mL ($\approx$ 3.5 nCi/g) for alpha-emitting plutonium isotopes (α-Pu). Tc-99 is also present at a maximum concentration of 0.321 μCi/mL. The concentrations of nuclei after solidification were not given, but about 20 gallons (75,700 mL) of waste is solidified per 71 gallon (2.68E+05 mL) drum. The maximum waste concentrations per drum can roughly be estimated at 0.18 μCi/mL for Cs-137, 0.04 μCi/mL for Sr-90, 0.09 μCi/mL for Tc-99, and 1.1 nCi/g α-Pu. Comparing this rough estimate to 10 CFR 61.55, Sr-90 is the only nuclei in greater than a Class A concentration (it would place the waste barely into the Class B range at its highest recorded observed concentration). The majority of the waste forms produced by this process are therefore Class A. Drums produced during the transition period (see Section 4.4.5) had higher α-Pu concentrations and, consequently, were Class C waste.

The waste characterization data appears to be complete for the process WVNS plans to use.

4.2 Minimum Requirements of 10 CFR 61.56(a)

Section 61.56(a) of 10 CFR Part 61 specifies minimum requirements for all classes of waste. These requirements are intended to facilitate handling at the disposal site and provide for the protection of health and for the safety of personnel at the disposal site.

4.2.1 Packaging

Section 61.56(a)(1) of 10 CFR Part 61 specifies that waste must not be packaged for disposal in cardboard or fiberboard boxes. At West Valley the waste form is contained in steel drums or liners and thus satisfies this requirement.

4.2.2 Liquid Waste

Section 61.56(a)(2) of 10 CFR Part 61 specifies that liquid waste must be solidified or packaged in sufficient absorbent material to absorb twice the volume of the liquid. The decontaminated sludge wash is solidified and, therefore, fulfills this requirement.

4.2.3 Free Liquid

Section 61.56(a)(3) of 10 CFR Part 61 specifies that free standing liquid in the solid waste shall not exceed 1% of the volume of the solid waste. Section 4.4.7 below describes how this requirement is met.

4.2.4 Reactivity of Product

Section 61.56(a)(4) of 10 CFR Part 61 specifies that the waste must not be readily capable of detonation or of explosive decomposition or reaction at normal pressures and temperatures, or of explosive reaction with water. The cement-solidified decontaminated sludge wash is not capable of such reactions and thus satisfies this requirement.

4.2.5 Gas Generation

Section 61.56(a)(5) of 10 CFR Part 61 specifies that 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. The solidified waste forms satisfy this requirement.

4.2.6 Pyrophoricity

Section 61.56(a)(6) of 10 CFR Part 61 specifies that the waste must not be pyrophoric or contain materials which are pyrophoric. Pyrophoric liquid or solid are defined in Section 61.2. The solidified waste satisfies this requirement.

4.2.7 Gaseous Wastes

This provision (10 CFR 61.56(a)(7)) is not applicable to the subject waste forms.

4.2.8 Hazardous Waste

Under the Resource Conservation and Recovery Act (RCRA), the U.S. Environmental Protection Agency (EPA) has jurisdiction over the management of solid hazardous wastes with the exception of source, byproduct, and special nuclear material, which are regulated by the NRC under the Atomic Energy Act. Low-level radioactive wastes (LLW) contain source, byproduct, or special nuclear materials, but they may also contain chemical constituents which are hazardous under EPA regulations promulgated under Subtitle C of RCRA. Such wastes are commonly referred to as mixed low-level radioactive and hazardous waste (mixed waste).

Applicable NRC regulations control the byproduct, source, and special nuclear material components of the mixed LLW (10 CFR Parts 30, 40, 61, and 70); EPA regulations control the hazardous component of the mixed LLW (40 CFR Parts 260-266, 268 and 270). Thus, all of the individual constituents of mixed LLW are subject to either NRC or EPA regulations. However, when the components are combined to become mixed LLW, neither agency has exclusive jurisdiction under current Federal law. This has resulted in dual regulation of mixed LLW, wherein NRC regulates the radioactive component and EPA regulates the hazardous component of the same waste.

Under Section 10 CFR 61.56(a)(8), waste containing hazardous, biological, pathogenic, or infectious material must be treated to reduce to the maximum extent practicable the potential hazard from the non-radiological materials. The waste form consisting of the cement binder material plus the waste streams described in Section 4.1 of this evaluation does not contain biological, pathogenic or infectious material, and thus satisfies these requirements of 10 CFR Part 61.

This review does not evaluate EPA requirements relating to hazardous solid waste. The QR states that the waste liquids contain chromium in concentrations that classify the liquids as hazardous. However, Toxicity Characteristic Leaching Procedure (TCLP) testing of the solidified waste product shows that the final waste form is not hazardous under EPA test methods.

4.3 Stability Requirements of 10 CFR 61.56(b)

The requirements of 10 CFR 61.56(b) are intended to provide stability of the waste. Stability is intended to ensure that the waste does not structurally degrade and affect overall stability of the site through slumping, collapse, or other failure of the disposal unit and thereby lead to water infiltration. Stability is also a factor in limiting exposure to an inadvertent intruder, since it provides a recognizable and nondispersable waste.

4.3.1 Structural Stability

According to 10 CFR 61.56(b) and 61.7(b)(2), the waste form must maintain its physical dimensions and its form for 300 years under the expected disposal conditions such as weight of overburden and compaction equipment, the presence of moisture and microbial activity, and internal factors such as radiation effects and chemical changes. The solidified waste product will be packaged in suitable containers, but the containers will be given no credit for stability. The evaluation for structural stability is discussed in Section 4.4 under recommendations of the 1991 Technical Position on Waste Form.

4.3.2 Free Liquid

Section 10 CFR 61.56 (b) (2) requires that wastes processed to a stable form have a liquid content that does not exceed 0.5 percent of the volume of the waste. The TP in Reference 4 Appendix A addresses this requirement. See Section 4.4.7, below.

4.3.3 Void Spaces

Section 61.56(b)(3) of 10 CFR Part 61 states that void spaces within the waste and between the waste and its package must be reduced to the extent practicable. Containers holding the processed waste form will be filled while the waste form is still fluid. Solidification then takes place in the container, thereby reducing the void spaces between the waste and the container to the extent practicable. Section 3.4 of the PCP specifies a minimum filling of drums of 85% during routine processing, which fulfills the requirement. During processing, one drum per process tank (which holds enough liquid waste for roughly 100 or 200 drums, depending on the tank used) is set aside and physically inspected, in part, for drum fill.

4.4 Recommendations of the Technical Position on Waste Form

The 1991 Technical Position on Waste Form (Ref. 5) recommends tests and criteria for demonstrating the stability called for in 10 CFR Section 61.56.

Stable low-level radioactive wastes are required to maintain their gross physical properties and physical identity for 300 years or more. Structural stability may be demonstrated by subjecting samples of the waste forms to a series of tests. The recommended tests include compressive strength, leach resistance, and resistance to biological attack, irradiation, thermal cycling, immersion in water, and correlation of lab-scale results with full-scale products, as demonstrated by compressive strength tests following these test exposures.

The following sections summarize the qualification testing of the cement-solidified decontaminated sludge wash waste forms as described in the Qualification Report. Test results are evaluated against the criteria recommended in Appendix A of the TP.

4.4.1 Compressive Strength

In Appendix A to the TP NRC specifies a minimum of 500 psi mean compressive strength for waste form specimens cured for a minimum of 28 days. In some cases 28 days may be inadequate for essentially complete curing of waste form specimens. Therefore, Appendix A recommends that sufficient specimens be prepared to determine the compressive strength increase with time to ensure that the specimens have attained near-maximum (i.e., at least 75% of the projected peak) compressive strength. The specimens tested using ASTM C39 procedures (Ref. 10) should be right circular cylinders 2 to 3 inches in diameter with length approximately twice the diameter. Because of the scatter inherent to compressive strength data for a brittle material such as cement, Appendix A specifies a minimum of ten specimens when determining the compressive strength.

XXX-044:

Cores were taken from XXX-044 surrogate sludge wash drums after 38, 42, and 74 days of cure. After like amounts of curing time, 20 wt%, 0.64 water-to-cement ratio (w/c) TDS XXX-044 cores showed slightly lower compressive strength than those from Campaign 22-1S. There is a slight, but not significant, increase in strength between 38 day (1202 $\pm$ 145 psi), 42 day (1305 $\pm$ 34 psi), and 74 day (1322 $\pm$ 147 psi) cores for the 20 wt% TDS XXX-044 drums, indicating an essentially cured condition at approximately 40 days cure.

Neat cement samples prepared in XXX-044 indicated complete curing after 28 days (i.e., no discernable trend in strength increase was observed). The 19 cores of neat cement showed average strength of 2510 $\pm$ 727 psi at a 0.65-0.66 w/c.

The strengths of the 19 cores with 14 wt% TDS ranged from 2377 $\pm$ 531 psi at 0.61 w/c, to 1688 $\pm$ 104 psi at 0.64 w/c. The 26 cores obtained from the three drums prepared at 20 wt% TDS indicated strengths of 2064 $\pm$ 405 psi for 0.61 w/c, and 1247 $\pm$ 135 psi for 0.64 w/c.

XXX-051:

XXX-051 drums were cored between 29 and 35 days, with the exception of Drum E which was cored at 33, 40, and 47 days of cure. This drum showed a slight, but insignificant, decrease in average compressive strength over this time period from 1757 $\pm$ 108 psi to 1670 $\pm$ 115 psi. No further testing was performed under XXX-051 that would indicate compressive strength time-behavior.

A total of 21 cores were taken from the top, middle, and bottom of seven drums. These drums were prepared with combinations of ingredients designed to span the operating range, and had w/c ranging from 0.62 to 0.66 and wt% TDS of 20, 24 and 27. As expected, cores with the lowest water to cement ratio and the lowest wt% TDS exhibited the highest compressive strengths for similar cure time. Compressive strengths ranged from 810 psi (24 wt% TDS, 0.66 w/c) to 2080 psi (20 wt% TDS, 0.66 w/c). Averaging the results of all cores yields an average as-cured compressive strength of 1495 $\pm$ 319 psi. The nominal recipe (20 wt% TDS, 0.66 w/c) yields a slightly higher average of 1857 $\pm$ 193 psi.

Campaign 22-1S:

All Campaign 22-1S testing was performed at the nominal recipe (20 wt% TDS, 0.66 w/c). Drum cores exhibited compressive strengths from 990 to 1960 psi. Compressive strength development in time was also monitored during Campaign 22-1S as cores from three drums were tested at 49, 50, 65, and 82 days. Cores from the same drum (drum no. 82112) were used for the 65 and 82 day tests, and it was noticed that the 65 day cores were noticeably damp, possibly due to incomplete curing. At 65 days drum 82112 had an average strength of 1140 psi, 70% of its strength 17 days later (i.e., at 82 days). The six 49 and 50 day cores (three each from two drums) exhibited an average strength of 1497 $\pm$ 200 psi.

The RAI detailed NRC concerns that comparison of drum 82112 results to that of other drums might not be an adequate method of demonstrating that the waste forms were 75% cured prior to initiation of qualification work. In the response to the RAI WVNS agreed with NRC that drum 82112 was behaving differently than other Campaign 22-1S drums. WVNS explained that drum 82112 was from the end of the "transition" period (see the discussion on transition drums in Section 4.4.5, below) and thus had a lower pH than the balance of Campaign 22-1S drums.

To resolve this concern, WVNS revised the QR to indicate a baseline compressive strength of 1497 $\pm$ 200 psi (the average of the six cores taken from drums other than 82112), and to clarify and justify why WVNS believed the specimens to have attained 75% of their ultimate compressive strength prior to the initiation of qualification testing. The as-cured strengths measured on the 6 individual cores are given in the first part of Table 4, in Section 4.4.5, below. WVNS also committed to using the results of long-term testing to better establish the 75% cured, baseline compressive strength.

Initial long-term test results have since been incorporated into Rev. 0 of the QR. Six cores taken after a curing period of 555 days, from the same drum which had been cored at 49 days (drum 82538), indicated compressive strength of 1488 $\pm$ 542 psi. Two of the six cores were substantially lower than the other four (i.e, 825 psi average versus 1820 average for the four others). This additional information provides strong evidence that specimens were essentially cured prior to the immersion test. In fact, even if the two lower-strength cores are arbitrarily excluded from the average, the 49/50 day strengths of the qualification drums exceed 75% of the 555 day compressive strength.

The exclusion of drum 82112 core results from computation of the baseline strength reduces the number of specimens below the TP recommended minimum of ten. However, NRC staff believes that the use of cores from actual production drums, the high compressive strengths exhibited by these cores, comparison of results to long-term testing, and consideration of results of tests done on surrogate waste in XXX-044, adequately address NRC concerns expressed by the RAI and the intent of the TP guidance. Basing the as-cured strength on the 6 cores is thus accepted.

In conclusion, all compositions tested had compressive strengths well in excess of the minimum 500 psi criterion called for in the TP, and the 49/50 day strengths are essentially the same as the 555 day values, indicating qualification work was performed on essentially cured specimens.

4.4.2 Radiation Resistance

Appendix A to the TP (Ref. 5) recommends that specimens of proposed waste forms containing ion-exchange resins or other organic materials should remain stable after exposure to an absorbed gamma ray dose of 10^8 rad. Irradiation testing need not be conducted on waste forms containing inorganic materials unless the expected cumulative dose for the corresponding actual waste forms is expected to exceed 10^9 rad. The irradiated cement waste form specimens should have a minimum compressive strength of 500 psi when tested in accord with ASTM C39 (Ref. 10) There should be no visual evidence of significant degradation of the specimen, e.g., no cracking or spalling, after the exposure to radiation.

The sludge wash does not contain ion-exchange media and the total organic carbon content is about 75 ppm, according to testing performed in response to the RAI and reported in the QR. The RAI response indicates that the total dose to the waste form will be much less than 10^8 rad. Organics had been used at West Valley during reprocessing operations, including kerosine, tributyl phosphate, mono- and di-butyl phosphate, and the decontamination reagents oxalate, tartrate, and citrate (Ref. 6). The high radiation levels in the tank have caused degradation of the great majority of these substances. Although previous experience with the supernatant cement recipe development (Ref. 6) indicated that the organic residues could be retarding set (a phenomena that led to the selection of admixtures), there is no indication that this concentration of organics would cause the waste form to be vulnerable to irradiation-induced degradation. Irradiation testing of the supernatant specimens indicated that they were not degraded (Ref. 11), even though the supernatant had higher levels of organics than the sludge wash. Based on previous data, the low organic carbon content, and the low total dose to the waste form, NRC had previously determined (Ref. 12) that irradiation testing is not warranted.

4.4.3 Biodegradation Resistance

Appendix A to the TP (Ref. 5) recommends that waste form specimens for waste streams containing carbonaceous materials be tested for resistance to biodegradation in accordance with both ASTM G21 (Ref. 13) and ASTM G22 (Ref. 14). These are tests for resistance of synthetic polymeric materials to degradation by fungi and by bacteria, respectively. No indication of culture growth should be visible. Following biodegradation testing, cement waste form specimens should have compressive strengths greater than 500 psi as tested using ASTM C39. There should be no visual evidence of significant degradation of the specimen, e.g., no cracking or spalling, after the biodegradation testing.

As stated in Section 4.4.2, above, the sludge wash contains only low concentrations of organic materials. The supernatant specimens were spiked with organics and subjected to biodegradation tests, and demonstrated satisfactory performance. Based on previous data and the low organic carbon content, NRC had previously determined (Ref. 12) that biodegradation testing is not necessary.

4.4.4 Leachability

The 1991 TP recommends that leach testing of cement-stabilized wastes be performed for 5 days in accordance with the procedure described in ANSI/ANS-16.1 (Ref. 15). In addition to the demineralized water specified in ANSI/ANS-16.1, Appendix A to the TP specifies that the specimens should also be exposed to a synthesized sea water leachant. The bulk of the leach testing should be performed with whichever of the two leachants is found to be more aggressive. An acceptable method of identifying the more aggressive of the two leachants is to perform 24 hour (or longer) leaching measurements on both leachants in order to determine which leachant results in a lower leach index (i.e., a higher leach rate.) The leachability index, as calculated in accordance with ANSI/ANS-16.1, should be greater than 6.0.

During Campaign 22-1S, three one-inch by three-inch cylindrical "mini-cores" from drum #82113 (20 wt% TDS) were tested for leach resistance in both demineralized water and synthetic seawater. Analysis of the leach solution focussed on four radionuclides: Sr-90, Tc-99, Cs-137, and α-emitting plutonium isotopes (α-Pu in the QR). The reported leach indices are all greater than 6. Leach indices are shown in Table 2, below and in Table 8 of the QR. QR Table 8 also gives confidence intervals and correlation coefficients as required by the ANSI/ANS 16.1 test.

Table 2
Leach Indices for Portland I Cement and Sludge Wash Waste Form

Radionuclide	Demineralized Water	Synthetic Seawater
Tc-99	7.8 $\pm$ 0.4	7.9 $\pm$ 0.4
Sr-90	11.5 $\pm$ 0.5	11.7 $\pm$ 0.5
Cs-137	7.7 $\pm$ 0.4	7.8 $\pm$ 0.5
α-Pu	14.4 $\pm$ 0.5	14.5 $\pm$ 0.5

There appear to be no significant differences in leach indices for the two leach solutions. Thus, neither demineralized water nor synthetic seawater can be considered more aggressive. The lowest leach index is 7.7 for Cs-137. The 20 wt% TDS solidified sludge wash exceeds the TP leach index criterion.

Results for the XXX-044 series drums are also presented in the QR (actually the results of XXX-026 leach testing). This testing involved laboratory-scale cylinders prepared with decontaminated supernatant waste, with a sodium sulfate spike and pH adjustment, as a simulated sludge wash liquid. Note that the 33 wt% TDS waste form recipe tested failed to qualify (though not because of its leach test performance). Reported leach indices are all greater than 6.0. Relevance of these data are not considered by this TER, as NRC staff believes results of Campaign 22-1S leach testing are sufficient to demonstrate adequate leach resistance for the 20 wt% TDS sludge wash recipe.

4.4.5 Immersion Resistance

Appendix A to the TP recommends that, following immersion in water for at least 90 days, waste specimens should maintain a minimum compressive strength of 500 psi as tested using ASTM C39. The water used should be the more aggressive of the two leachants identified during leach testing. The compressive strength after immersion should be at least 75 percent of the compressive strength measured before immersion. There should be no visual evidence of significant degradation, such as cracking or spalling, of the specimen after the 90-day immersion period.

Certain waste streams, containing bead resins, chelates, filter sludge, and floor drain wastes, can exhibit complex relationships between cure time and immersion resistance. For these Appendix A recommends additional immersion testing on specimens that have been cured in sealed containers for at least 180 days. This additional testing consists of at least 7 days immersion followed by 7 days drying in ambient air at a minimum temperature of 20°C. After drying, the specimens should meet the post-immersion compressive strength and visual criteria specified above. This test was performed by WVNS and the results are discussed in Section 4.4.10.2, below.

The immersion test appears to be the most stringent of the TP tests for the sludge wash-Type I Portland cement recipe. The high sulfate content of the waste stream seems to promote formation of ettringite causing an expansive decomposition of the waste form. Ettringite ($Ca_6Al_2(SO_4)_3(OH)_{12} \bullet 26H_2O$) is a crystalline mineral phase caused by and expansive reaction of alumina-containing hydrates with sulfate and calcium hydroxide, and is the most common reaction in sulfate attack of concrete (Ref. 16). For the sludge wash recipe, WVNS found that this effect is enhanced at waste pH values lower than 12.0. Another potential problem identified by WVNS is that coring of the drums and specimen removal appear to damage the structural integrity of some cores. However, cores are considered more representative than laboratory-scale samples, and therefore continue to be the preferred method of sampling.

XXX-044:

XXX-044 was issued in response to the failure in immersion of the XXX-026 qualification work (done at 32 wt% TDS), to test sludge wash recipes formulated with 0 wt% (neat cement), 14 wt%, and 20 wt% TDS. Testing was performed on both cylinders cast from scoop samples taken from full-scale drums before they set, and on cores taken from full-scale drums after a minimum 28 day curing period. Immersion testing was performed in both demineralized water and synthetic seawater.

Cylindrical specimens sampled from full-scale drums before they set were cured in the laboratory prior to being subjected to qualification testing. These samples did not retain their compressive strength during immersion, with the exception of the neat cement specimens. Differences in curing conditions, as compared to cored samples, are the speculated cause of failure of the specimens. Due to this failure, testing of cylindrical sampled specimens was discontinued (i.e., cores were used for all later tests).

Cored specimens of solidified surrogate sludge wash were taken for the 20 wt%, 14 wt%, and 0 wt% recipes. Enough specimens were created to allow 90 day immersion testing in both demineralized water and simulated seawater. Based upon pre- to post-immersion comparisons, simulated seawater was determined to be the most aggressive leachate. For the three 20 wt% TDS, 0.64 w/c cores in simulated seawater, a post-immersion compressive strength of 1189 $\pm$ 20 psi was observed, which represents a 5% decrease from as-cured average values. The greatest average loss of compressive strength occurred for the 20 wt% TDS, 0.61 w/c cores in simulated sea water, which lost an average of 18% of their compressive strength during immersion.

XXX-051:

Seven full-scale drums were produced at 20 wt%, 24 wt%, or 27% TDS. A sulfate spike was added to provide for an operating margin and increased the sulfate concentration in the waste on a dry salt basis by a nominal 25% (i.e., from 9.1 wt% to 11.3 wt% of total salts). The drums were cured 29-35 days, cored, and the cores were immersed in synthetic seawater (the most aggressive leachate from XXX-044 testing). Cores were photographed monthly for records.

After 30 days of immersion in synthetic seawater, visual examination of the cores indicated deterioration. An exception to the test procedure was granted to commence destructive testing prior to the completion of the 90-day immersion period. The post-immersion compressive strengths were significantly lower than the pre-immersion values and continued to decline as a function of the time immersed. Some samples deteriorated to the point of being unusable for meaningful compressive strength testing. A summary of the immersion test performance of these cores is given in Table 3.

Table 3. XXX-051 Immersion Test Performance

Core sample's wt% TDS, w/c ratio, Drum ID	Cure Time (days)	Immersion Time (days)	Pre-immersion Comp. Strength (psi, ave. of 3)	Post-immersion Comp. Strength (psi, ave. of 3)
27, 0.66 Drum A	29	90	1313	67
24, 0.66 Drum B	30	42	1097	590
24, 0.70 Drum C	33	89	1197	95
24, 0.66 Drum D	36	90	not scheduled	233
24, 0.62 Drum E	33	90	1757	63
24, 0.66 Drum F	34	65	1347	537[1]
20, 0.66 Drum G	35	90	1857	187

NOTES: [1] Cores from this drum were not suitable for ASTM C-39 testing per the requirements of that test, a number has been provided for information only.

The review of the performance of XXX-051 samples determined that the immersion test failure was possibly the result of one or more of the following factors: (1) low pH of the waste due to residuals in the liquid waste treatment system from supernatant solidification operations, (2) difficulties of dissolving the sulfate spike solution resulting in uneven sulfate distribution in the waste, (3) elevated temperatures (35°C) of ambient environment during the immersion test, and (4) an internal change in immersion test protocol which tripled the liquid-to-specimen volume-to-surface-area ratio to 30 cm. WVNS reported in the QR that X-ray diffraction analyses confirmed that post-immersion cores from XXX-051 contained higher concentrations of ettringite than a Campaign 22-1S sample.

Campaign 22-1S Transition Wastes:

The drums processed near the time of XXX-051 testing showed a gradual increase in pH that was a result of residuals in the evaporator and holding tanks from previous waste processing and acid rinses. Due to physical process restrictions, there are always some residuals left in the evaporator that are passed on to the next batch of waste. The lower pH of these drums is conducive to enhanced ettringite formation, creating a potential for failure in immersion similar to that observed in the original XXX-026 recipe mentioned above.

Because of schedule needs to process the sludge in the high level waste tank 8D-2 in a timely manner, WVNS began processing sludge wash with the 20 wt% TDS Portland Type I cement recipe prior to the completion of the XXX-051 immersion tests. (XXX-051 tests were viewed by WVNS as a confirmatory test of positive results of XXX-044 qualification work.) Production drums produced immediately after the XXX-051 drums (early Campaign 22 drums) showed a gradual increase in pH from 10.5 to 12.5 as the residuals effect on the pH gradually diminished. The Process Control Plan required monitoring of pH during processing, but this increase did not prevent decisions from being made to proceed with production. These production drums are the "transition drums".

Drum 82112, previously described in Section 4.4.1, was processed during the transition period. Cores from this drum taken at 65 days after casting were described as "damp" and showed considerably lower average compressive strength than cores taken from the same drum at 82 days of cure. The pH of this drum was 12.0, lower than the 12.4 to 12.6 of subsequent Campaign 22-1S processing. Cores from this drum were also subjected to immersion testing and showed significant visible degradation. Post-immersion compressive strengths were 320 and 280 psi, indicating a failure of the test.

NRC has concerns about the transition drums processed at the lower pH and their ability to successfully pass an immersion test. The 21 drums produced prior to XXX-051, the 11 drums from XXX-051, and the 176 drums succeeding XXX-051 comprise the transition drums. There are indications that the following 92 drums processed could also be transition drums, because of the higher alpha-Pu content of these drums as compared to subsequent Campaign 22-1S drums (the alpha-Pu content of these drums is more consistent with that of the supernatant waste).

Because of the difficulties in obtaining satisfactory compression strengths for the transition drums when representative samples were immersed, their ultimate disposition is questionable and needs to be addressed by DOE. This TER does not make a conclusion as to the stability of the 208 or 300 known transition drums described in this section, and NRC considers this an outstanding issue.

Campaign 22-1S Qualification Cores:

Cores were taken from one Campaign 22-1S production drum (drum 82538) after the failure in immersion of the XXX-051 drums. The RAI requested justification on the choice to only test cores from a single drum, and questioned how representative cores from a single drum are, given the thousands of sludge wash drums produced. In response to the RAI, WVNS stated: (1) Campaign 22-1S cores were expected to exhibit immersion test behavior similar to that of XXX-044 cores, and were thus viewed as a confirmatory test, and (2) tight process controls that exist, and the consistency of the waste stream, sufficiently ensure that one drum is representative of all sludge wash processing. The staff accepts this explanation.

Nine (9) cores were removed from the top, middle, and bottom positions of drum 82538 (20 wt% TDS, 0.66 w/c) and subjected to immersion testing in simulated sea water. These immersion tests were performed at ambient laboratory temperatures with a liquid-specimen volume-to-surface area ratio of 10 cm (as opposed to 30 cm of XXX-051 tests).

This drum cured 49 days prior to initiation of the immersion test. In response to the RAI, WVNS committed to establishing that this drum was essentially cured prior to the initiation of immersion testing. As discussed above in Section 4.4.1, WVNS has satisfactorily addressed this concern.

The pre- and post- immersion test results for this drum are presented in Table 4, below. After immersion, cores exhibited minor, superficial cracking. Results indicate that the average strength after immersion decreased by 18% from 1497 psi to 1230 psi. Samples from the middle portion of the drum indicated a decrease in strength greater than that allowed by the TP (i.e., decrease of 25% or more). In fact, the sample demonstrating the lowest compressive strength (1030 psi) is only 60% of the corresponding pre-immersion strength from drum 82538 of 1720 psi. WVNS was requested to assess this performance by the staff's RAI. WVNS responded to the RAI by indicating that it is inappropriate to compare compressive strength results from individual cores due to the large statistical variations frequently observed when crushing brittle materials such as cement. The staff accepts this position and this issue is considered resolved.

Table 4. Campaign 22 1-S Drum Immersion Test Performance

Test Condition	Core Location & Comp. Strength, psi			
	Top	Middle	Bottom	Average
Pre-Immersion				
49/50 days (as-cured strength from 2 drums)	1680	1720	1410	1497
	1560	1420	1190	
Post-Immersion				
43 days	1290	1490	----[1]	1390
60 days	1560	1180	1500	1413
90 days	1410	1030	1250	1230

Notes: [1] This core was not subjected to ASTM C-39 compressive strength testing

The extensive immersion testing program performed by WVNS exceeds that recommended in Appendix A of the TP. Adequate evidence exists to conclude that the 20 wt% sludge wash recipe prepared at nominal 0.66 W/C produces waste forms that perform sufficiently during the immersion test, provided that strict PCP limits are observed on key variables such as pH and sulfate content.

4.4.6 Thermal Cycling

Appendix A to the 1991 Rev. 1 TP recommends that thermal cycling tests be conducted in heating and cooling chambers conforming to those described in ASTM B553 (Ref. 17). Thirty thermal cycles between 60°C and -40°C should be carried out, but in a manner which allows the specimens to come to thermal equilibrium at the high and low temperature limits. There should be no visual evidence of significant degradation of the specimen, e.g., no cracking or spalling, after the thermal cycling. Following testing, the specimens should have compressive strengths greater than 500 psi as tested using ASTM C39.

Thermal cycling was performed as part of qualification testing under WVNS-XXX-051 at 24 wt% TDS. It was not scheduled for the Campaign 22-1S drums, and was abandoned under TP-044 after cylinders and cores demonstrated dissimilarity during immersion testing. Although no thermal cycle testing was performed using the nominal (i.e., Campaign 22-1S) recipe, WVNS states that positive results from the XXX-051 tests combined with positive results from thermal cycling of lab scale cylinders prepared under test series XXX-026 (33 wt% TDS simulated waste), bound the nominal recipe and thus provide sufficient evidence that the nominal recipe will perform satisfactorily during thermal cycling.

Under XXX-051, three 3"x6" cores were subjected to thermal testing. The cores were taken from the top, middle, and bottom of a drum with 24 wt% TDS and a 0.66 water to cement ratio. This exceeds the nominal recipe's 20 wt% TDS. WVNS asserts that thermal-cycle test performance of 20 wt% TDS samples would not significantly differ from that of the 24 wt% TDS XXX-051 drums. NRC staff agrees with this position, and based on previous results of thermal cycle testing for the supernatant and sludge wash recipes, has therefore determined that thermal cycle testing of Campaign 22-1S drums is not warranted.

The curing time before testing is not explicitly stated, but WVNS-TSR-051 mentions a minimum 28 day cure. After cycling, the cores' compressive strengths were 930 psi for the core taken from the top of the drum, 1390 psi for the middle core, and 1180 psi for the lower core, for an average of 1167 $\pm$ 230 psi. Additionally, no spalling or cracking was observed. The criterion of a minimum 500-psi compressive strength after thermal cycling was exceeded, and stability when subjected to thermal cycling has been demonstrated.

4.4.7 Free Liquids

Section 10 CFR 61.56 (b) (2) requires that wastes processed to a stable form have a liquid content that does not exceed 0.5 percent of the volume of the waste. The TP, Appendix A addresses this requirement. Appendix A recommends that waste specimens have less than 0.5 percent by volume of the waste specimen as free liquids as measured using the method described in ANS 55.1 (Ref. 18). Free liquids should have a minimum pH of 9, which is considered representative of the alkaline properties of cement.

The Qualification Report describes an alternative method used by WVNS to detect free liquids involving a two-step testing approach. First, during processing, 2" cubes are prepared from each batch of waste under the Process Control Plan prior to solidification of full-scale drums. These verification cubes are discussed in Section 4.4.10.2 of this report. The cubes are limited to no "bleed water" after 24 hours of cure in an oven. The second method was to examine full-scale specimens produced during qualification work. It was noted that no free liquids were observed after 24 hours cure, and that only superficial liquid existed after 1 hour of cure. Section 8.0 of the PCP requires that one random drum per process tank be set aside and examined to verify absence of free liquids following a 3 day cure.

These methods provide equivalent assurance to the TP recommended procedure, and sufficiently show that the solidification process meets the free liquid criterion of the TP and 10 CFR 61.56.

4.4.8 Full-Scale Specimen Test Results

Appendix A to the TP (Ref. 5) recommends that test data from sections or cores of the anticipated full-scale products should be obtained if small, simulated laboratory-size specimens are used for the TP qualification testing. Full-scale test data are to be used to demonstrate that the characteristics of actual size products correlate with those of simulated laboratory-size specimens. Non-radioactive full-scale specimens can be used, but they should be fabricated using actual or comparable solidification equipment. The correlation should be established by performing (1) compressive strength tests on material cured for at least 28 days, and (2) 90-day immersion followed by compressive strength tests for the waste that is most difficult to solidify. Appendix A also recommends that samples from full-scale specimens should be destructively analyzed to ensure that the product is homogeneous to the extent that all regions of the product can expect to have compressive strengths of at least 500 psi.

The Campaign 22-1S qualification program used cores from full-scale drums after cure times of 49 or 50 days. These full-scale specimens had been processed in the Cement Solidification System from actual sludge wash liquids. The core samples for the test program were obtained from top, middle and bottom locations in the drums, and showed no significant differences in compressive strength attributable to location.

Two production drums from Campaign 22-1S were monitored for temperature changes during curing. The top and central portions of the drums consistently reached higher temperatures than the bottom portions (about 85°C versus 60°C), as shown in Figures 8 and 9 of the QR. All qualification work was performed using cores from all three regions of drums.

There was no discernable difference in the test performance between cores taken from the three regions, and all Campaign 22-1S cores have exceeded the 500 psi minimum compressive strength. The TP criterion for full-scale specimen tests to confirm processed waste homogeneity was met and exceeded.

4.4.9 Qualification Test Specimen Preparation

Appendix A to the TP recommends that certain precautions be taken regarding the ingredients, mixing, curing and storage of qualification test specimens as follows:

> Ingredients - The surrogate wastes used for qualification testing should simulate the actual wastes intended to be stabilized with the binder material under consideration. For example, the characterization parameters used to characterize the actual waste, namely, major constituents, density or specific gravity, pH, temperature, and minor ingredients, should, for the surrogate wastes, bracket or envelope those of the corresponding actual waste to the extent practicable, and where differences exist, the potential significance of such differences should be discussed.
>
> Mixing - In preparing laboratory-sized qualification test specimens, it should be shown by analysis and/or testing that the type of equipment used, the mixing time, the speed of the mixer, etc., will, in combination, impart the same degree of mixing to the laboratory specimens as the full-scale mixing equipment will impart to full-scale waste forms, and that the degree of mixing is sufficient to ensure production of homogeneous waste forms.
>
> Curing - (1) To ensure that the laboratory specimens endure curing conditions reasonably similar to those of the full-size products, the waste-form centerline temperature profile as a function of time should be obtained for the largest full-sized waste form to be qualified for each waste stream. That profile should be duplicated to the extent practical in the laboratory specimens, for example, by oven curing for a time period equivalent to the peak heat of hydration period. (2) Care is needed in formulation to preclude temperatures at or above the boiling point of the pre-solidification mix. (3) Sufficient test specimens should be prepared to determine the compressive strength increase with time in order to ensure that the qualification testing is performed on essentially cured

specimens as evidenced by a compressive strength greater than 75% of the projected peak compressive strength.

Storage - In order to simulate the environment within a typical full-scale waste form liner and to prevent loss of water which might affect the performance of specimens during subsequent testing, the qualification test specimens should be kept in sealed containers during curing and storage prior to testing.

WVNS conducted its qualification test program using cores from specimens prepared under full-scale production conditions, with actual wastes in XXX-051 and with simulated waste in XXX-044. Additional qualification work was performed using cores from actual production drums, during Campaign 22-1S. This meets the criteria of concern in this section.

4.4.10 Process Control Plan

A Process Control Plan (WVNS-PCP-002) was prepared by WVNS for controlling waste form production. In addition to providing the PCP for review, WVNS included in its Qualification Report a discussion of applicable TP criteria. This TER evaluates Rev. 9 of the PCP, which was produced by WVNS in response to the staff's RAI, and was issued August 23, 1995.

4.4.10.1 Process Parameters

According to Appendix A to the 1991 Rev. 1 TP, for each LLW formulation, the generic PCP should identify and restrict, within acceptable bounds, the following variables which influence the process and affect the product:

* Type of waste, for instance, bead resin, powdered resins, boric acid, sludge;

* Waste characteristics which affect solidified waste properties, such as pH, oil content, chelating agents, water content, minor constituent concentration limits;

* Solidification binder components and additives, e.g., type of cement, water, lime, silica fume, fly ash, furnace slag, and their order of addition; and

* Physical process parameters, e.g., maximum temperature, mixing equipment required, mixing speed and curing times.

Appendix A to the TP also specifies that the PCP provide certain other process information:

* How representative samples of the feed waste are to be obtained for preparing PCP verification and surveillance specimens;

* Typical and maximum batch sizes;

* The number of PCP specimens to be taken for each batch; and

* Where and how out-of specification process parameters are dealt with.

The WVNS PCP lists two sets of items for controlling the process. The first set, identified as product requirements, are necessary for producing an acceptable waste form. Product requirements are:

* water/cement ratio,
* TDS (wt%) of sludge wash solution,
* sulfate concentration in sludge wash solution,
* sludge wash solution pH,
* drum percent volume filled,
* free water in drum, and
* verification sample compressive strength.

Process requirements are necessary for smooth operation of the Cement Solidification System, and include:

* mix time,
* recipe additive additions,
* gel time of verification sample, and
* automatic data base updates.

If there are upsets in either set of requirements, the suspect drum is set aside for further evaluation, done on a case-by-case basis. Product requirement upset evaluations will include compressive strength tests and leachability tests. Process requirement upsets will involve a technical evaluation to determine product acceptability. In cases where a solidified waste drum is found not to be acceptable for disposal, Section 3.3 of the PCP specifies removing the drum from storage and placing it in a high-integrity container prior to disposal.

WVNS has the option of using one of two process tanks to store waste during operation of the cement solidification system (CSS). The CSS processes waste in batches of approximately 5,000 gallons if tank 5D-15A1 is used, or 10,000 gallons if tank 5D-15A2 is used. One sample is extracted from the tank being used prior to processing, and one additional sample is taken if tank 5D-15A1 is being used (when that tank is half full). Since there is nominally 20 gallons per mixer batch and two mixer batches per drum, this results in one verification cube representing approximately 125 drums produced. Additionally, one drum per processed tank is set aside and examined for freeboard/fill volume, gel time, and free liquids content.

Waste sampled from the staging tank is tested for density (from which wt% TDS is calculated), pH, radionuclides, and sulfate concentration. The data from this analysis is used to choose a solidification recipe from the limited set available. The recipe is chosen based on the wt% TDS value. A complete set of recipes is shown in Tables A1-1 to A1-6 in the PCP. When the recipe is chosen, a verification specimen is prepared and observed for gel time, and after 24 hours, crushed for compressive strength measurements. Full-scale solidification of the 5,000 gallon batch is initiated only if the compressive strength of the verification sample is within specification for that recipe.

4.4.10.2 Short-term (24 hour PCP Verification) Specimens

According to Appendix A of the TP, verification specimens must be prepared prior to a particular waste solidification campaign at a specific power plant. Actual waste should be solidified using the recipe qualified in laboratory testing for that waste stream. Mixing conditions of the waste with the cement and additives should duplicate to the extent practical full-scale mixing. Verification specimens should be cured under conditions (especially temperature-time profiles and relative humidity) similar to those used in the laboratory qualification test program. These short-term (24-hour) PCP verification specimens should be free of significant visible defects, exhibit less than 0.5% free liquid by volume. Within 24 hours after preparation, PCP specimens should exhibit a compressive strength within two standard deviations of the mean compressive strength obtained at 24 hours for test specimens from the associated laboratory qualification test program for the waste formulation. Compressive strength may be determined by ASTM C39 or by an alternative penetrometer method as described in Appendix A.

The PCP gives procedures for the preparation of verification specimens. The verification specimens are 2-inch cubes which are observed for gel time, set time and free liquid. After 24 hours in an oven, cubes are tested for compressive strength. Although cubes are not recommended in the TP for compressive strength testing, they are an acceptable geometry since WVNS developed a significant data base of cube strength measurements at 24 hours oven cure time as part of qualification work in test series XXX-053. This work established the PCP minimum cube compressive strength for waste compositions from 19 wt% to 21 wt% TDS, and results are shown in the Qualification Report Table 10. The strength obtained from an individual verification specimen is compared to the PCP minimum strength, as determined in XXX-053, prior to making a determination to initiate CSS operations for each batch.

NRC staff, in the RAI, disagreed with the method of determination of the PCP minimum strength in XXX-053. This method involved the preparation of 10 cubes with the nominal recipe (i.e., 20 wt% TDS, 0.66 w/c) and 20 other cubes with slight variations from the nominal recipe. The intent of selecting the variations was to capture the anticipated range of operating conditions during processing. Analyses of XXX-053 compressive strength results indicated that samples having slightly higher wt% TDS loadings or those having higher water-to-cement ratios exhibited markedly lower strengths than the nominal recipe samples. The TP recommends that the PCP specimen minimum acceptable strength be established by calculating the average value obtained with qualifications specimens and subtracting two standard deviations of that average. For XXX-053 this value was determined to be 383 psi (i.e., average of 792 psi, and standard deviation of 204 psi). Because of averaging of different recipes, the standard deviation calculated in XXX-053 was large, and consequently the average-minus-two-sigma level was too low, in NRC staff's opinion, to provide sufficient control of product during production.

WVNS responded to this NRC comment in the response to the RAI, and committed to establishing a more appropriate PCP minimum cube compressive strength. In Rev. 0 of the QR, WVNS describes a revision which increases the PCP minimum strength from 383 psi to 471 psi. The 471 psi value is based upon five cubes prepared in XXX-053 at 21 wt% TDS and 0.68 w/c ratio. This condition represents the maximum wt% TDS and maximum w/c ratio allowed by the PCP, and is therefore viewed as a "worst case" waste form.

Redefining the PCP minimum compressive strength necessitated review of the cube strengths of all production batches produced to that point. It was discovered that only one PCP cube strength (which was 428 psi) did not exceed the revised PCP minimum cube strength (471 psi). However, procedures in place at the time of that batch required preparation of three cubes per process tank, and the three cube average (508 psi) for that batch exceeded the revised PCP minimum. Since Section 5.9 of the PCP allows for the preparation of a second cube when the PCP minimum cube strength is not met the first time, the use of the three-cube average is acceptable to NRC staff and this event is not viewed as a process upset of the 471 psi limit.

NRC staff believes that the issue of identifying the PCP minimum strength needs further consideration. The proposed PCP minimum cube strength (471 psi) is based upon the average of five cubes. The TP recommends a minimum of ten specimens for this determination. There *were* 10 cubes created in XXX-053 at the nominal recipe (20 wt% TDS, 0.66 w/c). Test results from the nominal recipe would be the best to use for process control, in the staff's opinion, because the great majority of (meaningful) qualification work was performed using this recipe. However, the PCP minimum strength using these 10 cubes would be 542 psi, and Figure 7 of the QR shows that around 5 or 6 cubes (each representing about 125 drums) would fall below this limit.

WVNS has been notified that NRC staff is still concerned with this issue. NRC staff has indicated to WVNS that an acceptable resolution could be to use the 471 psi PCP minimum compressive strength, but to add to the long-term testing program results from additional testing of production drums which were prepared from batches showing low (e.g., less than about 500 psi) verification cube strength. This approach would be expected to verify high compressive strengths in these drums because of their long curing time. To resolve this issue, WVNS submitted a letter to NRC, dated March 6, 1995 (Ref. 19), in which WVNS committed to testing cores from a drum produced from a batch showing the lowest PCP minimum compressive strength (i.e., 476 psi). The one-time test will be performed in accordance with the long-term test program, and results will be submitted to NRC. NRC staff accepts this proposal and positive test results will close this issue.

4.4.10.3 Long-term Surveillance Specimens

For certain "problem" waste streams (in particular, bead resins, chelates, filter sludge, and floor drain wastes), the TP, Rev. 1, suggests that sufficient PCP specimens should be prepared to permit the retention, examination and testing of surveillance specimens as described in Appendix A. The surveillance specimens should be stored at room temperature in sealed containers. The purpose of the surveillance specimens is to provide confirmation that the waste forms are performing as expected.

The PCP does not give procedures for the preparation of surveillance specimens. The sludge wash waste is not one of the "problem" waste streams mentioned in TP Appendix A as requiring a surveillance program. However, WVNS has committed to a long-term monitoring and compressive strength test program, and submitted a long-term test plan to NRC (Ref. 20) December 10, 1993.

NRC staff and its contractor have reviewed the long-term test plan submitted by WVNS, and found that the long-term test program proposed by WVNS conforms to or exceeds the recommendations of the TP in the following respects:

* An adequate number (3) of specimens are compression strength tested at six-month intervals for five years,

* Three extra core samples are obtained for archiving and future examination,

* The surveillance specimens are obtained from actual waste drums (they are not PCP specimens), and all curing occurs in the drum, and

* The immersion tests and subsequent compression strength testing on single core samples will continue at six-month intervals for five years.

The TP suggests that compressive strength of surveillance specimens be compared to that obtained from qualification specimens cured for an equivalent period of time. The WVNS program calls for comparison to the as-cured Campaign 22-1S qualification testing compressive strength (i.e., 1497 psi). This deviates from the TP recommended practice because WVNS qualification work was performed on cored specimens from actual waste. Hence, the long-term test program in effect will monitor the changes, if any, in the waste product compressive strength for a five year period. This in turn will provide sufficient assurance that the waste forms are behaving like ordinary Portland cement, which exhibits constant or slowly increasing compressive strength for several years after it is cast (Ref 21).

At the time of the writing of this TER, results of the long-term test program were incomplete, but initial long-term test results have been submitted to NRC (Ref. 22). Cores were taken from a drum produced with 20.04 wt% TDS, 0.66 w/c, and subjected to compression testing and a 14 day immersion test. The cores were visually observed to be in good condition. The average strength of three cores was found to be 2210 psi. The mean strength of the specimen after the immersion test was found to be 1720 psi. Six cores taken after a curing period of 555 days, from the same drum which had been cored at 49 days (drum 82538) during qualification work, indicated compressive strength of 1488 $\pm$ 542 psi. The 49/50 day qualification baseline compressive strength was 1497 psi. The initial results meet the requirements established by WVNS' long-term test program.

5. CONCLUSIONS

Based on the information and favorable results that have been provided in the Qualification Report and Process Control Plan, NRC staff concludes that there is reasonable assurance that cement solidification of decontaminated sludge wash with Type I Portland cement will meet the waste form stability requirements of 10 CFR Part 61 and fulfills or exceeds the provisions of NRC's Technical Position on Waste Form (Rev. 1). This conclusion is predicated on the expectation that test results from the long term test program will continue to be acceptable, and will confirm the attainment of satisfactory compression strengths and stability performance of the cement solidified decontaminated sludge wash waste. It is the understanding of NRC staff that DOE will keep NRC fully informed of the results from the long term test program and provide, as a minimum, the results and evaluation on an annual basis until the program is completed.

Full concurrence with this conclusion is dependent on the resolution of two unresolved issues:

Because of the difficulties in obtaining satisfactory compression strengths for the transition drums when representative samples were immersed, their ultimate disposition is questionable and needs to be addressed by DOE. This TER does not make a conclusion as to the stability of the 208 or 300 known transition drums described in Section 4.4.5, and NRC considers the ultimate disposition of the transition drums an outstanding issue.

WVNS needs to demonstrate the quality of drums produced during Campaigns 22-1S, 23-1S, and 24-1S, for which the verification cube compressive strength was near the PCP minimum compressive strength (e.g., below about 500 psi), as discussed in Section 4.4.10.2, above. Staff has determined that the additional testing identified by WVNS in Reference 19 is an acceptable approach to resolving this issue.

6. REFERENCES

1. Waste Form Qualification Program for Solidification of Sludge Wash Liquid with Type I Portland Cement, West Valley Nuclear Services Company, Inc., for the U.S. Department of Energy, West Valley Demonstration Project, Volume 2, Issued August 24, 1994.

2. Technical Evaluation Report, Waste Form Qualification Program-Volume 3, Cement Solidification of Sludge Wash Liquid With Type V Portland Cement, West Valley Demonstration Project, U.S. Nuclear Regulatory Commission, March 1995.

3. Technical Position on Waste Form, Rev. 0, U.S. Nuclear Regulatory Commission, May 1983.

4. Workshop on Cement Stabilization of Low-Level Radioactive Waste, U.S. Nuclear Regulatory Commission and National Institute of Standards and Technology, NUREG/CR-0103, NISTIR 89-4178, October 1989.

5. Waste Form Technical Position, Rev. 1, U.S. Nuclear Regulatory Commission, January 24, 1991.

6. WVNS Experience with Cement Solidification of Decontaminated Spent Fuel Waste, C.W. McVay, J.R. Stimmel, and S. Marchetti, pp.41-56 in Workshop on Cement Stabilization of Low-Level Radioactive Waste, U.S. Nuclear Regulatory Commission and National Institute of Standards and Technology, NUREG/CR-0103, NISTIR 89-4178, October 1989.

7. White Paper - Removal of Plutonium from West Valley High-Level Liquid Waste, L.A. Bray, F.T. Hara, and T.F. Kazmeirczak, Draft C., January 1991, attached to letter, February 4, 1991, from W.F.MacKellar, WVNS, to T.J. Rowland, West Valley Project Office, DOE.

8. Letter with Subject: Request for Additional Information for "Waste Form Qualification Program for Cement Solidification of Sludge Wash Liquid with Type I Portland Cement," from John O. Thoma (NRC) to T.J. Rowland (WVPO), August 19, 1993.

9. Letter with Subject: WVDP Response to NRC Request for Additional Information on Type I Portland Cement Waste Qualification Program, from T.J. Rowland (WVPO), to J.O. Thoma (NRC), November 16, 1993.

10. Standard Test Method for Compressive Strength of Cylindrical Concrete Specimens, ASTM C39-84, American Society for Testing and Materials, 1985 Annual Book of ASTM Standards, Vol. 4.02.

11. Technical Evaluation Report on the Cement Solidification of the Decontaminated Supernatant Waste for the West Valley Project, U.S. Nuclear Regulatory Commission, November 29, 1988.

12. Letter with Enclosure: Review Comments on January 1991 WVNS Development of a Cement Waste Form For Decontaminated Tank 8D-2 Sludge Wash, from R. Davis Hurt (NRC) to T.J. Rowland (WVPO), April 22, 1991.

13. Standard Practice for Determining Resistance of Synthetic Polymeric Materials to Fungi, ASTM G21-70, American Society for Testing and Materials, 1981 Annual Book of ASTM Standards, Part 41.

14. Standard Practice for Determining Resistance of Plastics to Bacteria, ASTM G22-76, American Society for Testing and Materials, 1981 Annual Book of ASTM Standards, Part 41.

15. Measurement of the Leachability of Solidified Low-Level Radioactive Wastes by a Short-Term Procedure, ANSI/ANS-16.1 - 1986, American Nuclear Society, La Grange Park, IL (1986).

16. Interferences Mechanisms in Waste Stabilization/Solidification Processes, U.S. Army Engineer Waterways Experiment Station for the U.S. Environmental Protection Agency, EPA/600/2-89/067, January 1990.

17. Standard Test Method for Thermal Cycling of Electroplated Plastics, ASTM B553-79, American Society for Testing and Materials, 1981 Annual Book of ASTM Standards, Part 9.

18. American National Standard for Solid Radioactive Waste Processing System for Light Water Cooled Reactor Plants, ANSI/ANS-55.1 - 1979, American Nuclear Society, La Grange Park, IL (1979).

19. Letter with Subject: Nuclear Regulatory Commission (NRC) Requested Additions to Sludge Wash Cement Waste Long-Term Test Program, from T.J. Rowland (WVPO) to Gary C. Comfort (NRC), March 6, 1995. (Attachment A addresses Type I Portland Cement Recipe).

20. Long-term Compressive Strength testing of the Sludge Wash Liquid/Portland Type I Cement Waste Form, West Valley Nuclear Services Company, Inc., for the U.S. Department of Energy, West Valley Demonstration Project, WVNS-TRQ-062, Issued December 10, 1993.

21. The Chemistry of Cement and Concrete, 3rd Ed., F.M. Lea, Edward Arnold, London (1970).

22. Letter With Subject: Transmittal of Results from the First Long-Term Tests of Decontaminated Sludge Wash Cement-Waste With Type I and Type V Portland Cement, with Enclosures, from T.J. Rowland (WVNS) to G.C. Comfort (NRC), July 22, 1994.

Enclosure 2

TECHNICAL EVALUATION REPORT
WASTE FORM QUALIFICATION PROGRAM - VOLUME 3
CEMENT SOLIDIFICATION OF SLUDGE WASH LIQUID
WITH TYPE V PORTLAND CEMENT
WEST VALLEY DEMONSTRATION PROJECT

Prepared by the U.S. Nuclear Regulatory Commission
Office of Nuclear Material Safety and Safeguards
Division of Waste Management

MARCH 1995

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1. INTRODUCTION

The United States Department of Energy (DOE) is conducting a cleanup of stored high-level radioactive waste at the Western New York Service Center in West Valley, New York. The West Valley Demonstration Project Act of 1980 established the project and requires the DOE to consult with the Nuclear Regulatory Commission (NRC) on these activities. Low-level radioactive waste (LLW) produced by the project during the cleanup is being processed for ultimate disposal. DOE has been conferring with the NRC on a variety of aspects of the disposal of LLW at the Service Center.

The DOE has provided the NRC with the information and data on the cement solidification of the sludge wash liquids in a report entitled "Waste Form Qualification Program for Solidification of Sludge Wash Liquid with Type V Portland Cement, Volume 3" (Ref. 1). The DOE document describes the qualification test program and the process control plan (PCP) that uses Type V Portland Cement as the solidifying agent. The qualification test program consists of sample preparation and tests performed on the solidified product, while the PCP ensures that the procedures for the solidification of the waste are controlled within qualified process parameters. This NRC Technical Evaluation Report (TER) evaluates the cement-solidified sludge wash waste form being produced by DOE against the structural stability requirements for waste forms set forth in the Federal regulations in 10 CFR Part 61.

In May 1983, the NRC provided guidance (Ref. 2) to waste generators and processors for meeting the stability requirements of 10 CFR Part 61 by issuing the Technical Position on Waste Form (TP). The TP stated that structural stability could be achieved by processing (or solidifying) the waste or by placing the waste in a container (for instance, a high integrity container) or structure. Since the initial issuance of the TP, NRC staff have provided additional guidance to address troublesome issues uncovered in solidification operations. As an example, cement is commonly used to stabilize LLW; however, field experience and laboratory testing indicated that unique interactions can occur between the cement constituents and some components present in the waste materials which degrade the stability of the product waste form. Because of these experiences, the structural stability of the portland-cement-based waste forms was the major topic of discussion at a workshop on the cement solidification of LLW (Ref. 3). Subsequently, the NRC revised the TP in January 1991 (Ref. 4) and included Appendix A dealing with qualification testing, performance confirmation, and reporting of mishaps for cement-based waste forms.

This TER by the NRC staff evaluates the documents submitted by West Valley Nuclear Services (WVNS), the contractor conducting the radioactive waste operations for DOE at the West Valley site. The purpose of this review is to determine whether or not the cement solidification of the sludge wash by the process described in these documents using Type V cement meets the structural stability provisions of 10 CFR 61.56 and the relevant portions of the TP (Rev. 2), including Appendix A on LLW stabilization with cement. The next two sections provide a short history of LLW stabilization at West Valley and a brief description of the documents supplied by WVNS. Section 4 presents the NRC's staff evaluation as to whether the proposed test plans and procedures will assure the production of waste forms that meet the long-term structural stability criteria. Conclusions are summarized in Section 5. NRC's contractor, Brookhaven National Laboratory, assisted in the technical review of the DOE documents and was a major contributor to the findings in this TER.

2. BACKGROUND

The largest volume of liquid LLW processed at West Valley resulted from the treatment of the high-level waste liquids and sludges contained in Tank 8D2. This supernatant was passed through zeolite beds to remove Cs-137, the major radionuclide contaminant, from the supernatant. The effluent from the zeolite beds, the so-called "decontaminated" supernatant, still contained some activity and was solidified in cement.

Before the initial processing of decontaminated supernatant, WVNS developed a Portland I cement binder recipe using a simulant of the supernatant. Tests in the full-scale production facility yielded a product with entrained air, low density, and a lower-than-expected compressive strength. These problems were corrected by adding an antifoaming agent. Subsequent small scale tests with actual decontaminated supernatant indicated the presence of set retarders, probably organic chelating agents or their degradation products acting in conjunction with chromate ion. Calcium nitrate and sodium silicate additives counteracted the effects of the set retarders so that an acceptable waste form could be produced (Ref. 5).

With the supernatant processing completed, the next planned phase was the washing of the sludge now at the bottom of Tank 8D2. This sludge consisted of a layer of solids composed of insoluble oxides, hydroxides and carbonates as well as sodium sulfate (Na_2SO_4). To wash the sludge layer, water was added to the tank and recirculated to dissolve the Na_2SO_4. Sulfate must be removed before the sludge layer can be vitrified, since sulfates would separate from the molten glass. During laboratory-scale testing of the sludge wash process, substantial quantities of plutonium and uranium compounds were released into solution, indicating the potential for producing transuranic waste rather than LLW. An alternative decontamination technique consisting of pH control of the sludge wash water in conjunction with use of a titanium-coated IE-96 ion exchange medium was developed to remove the bulk of the cesium, plutonium, and strontium from the sludge wash (Ref. 6). Three washing cycles were planned originally, however, only two were conducted. The liquid collected from each wash was evaporated to reduce waste volumes, then solidified in cement.

The first approach to stabilizing the decontaminated sludge wash involved solidifying it with Portland I cement and various additives. A limited campaign produced several hundred drums at the same time that TP testing was conducted on cores from the first few drums produced. During the course of the testing, it was realized that the required waste loading for an acceptable waste form was lower than expected. This would have resulted in too many drums being produced, exceeding the capacity of the drum storage facility. There were also some questions about the performance of the Portland I cement based waste forms after the 90-day immersion test. To address this concern, WVNS then developed a process recipe based on Portland V cement which allowed a higher waste loading. The purpose of this TER is to evaluate the ability of the Portland V recipe to meet 10 CFR Part 61 stability requirements by surpassing the TP tests and criteria. A separate TER has been prepared by the NRC staff to document and evaluate WVNS efforts to solidify the decontaminated sludge wash using Type I Portland cement and other additives.

3. SUMMARY OF REVIEWED DOCUMENTS

WVNS has submitted a series of documents in a looseleaf binder format in Reference 1. Two of these documents, summarized below, were reviewed in detail. Other documents, such as "Test Requests," "Test Procedures," or "Test Summary Reports," provided more specific details of how data were produced to support the Qualification Report and Process Control Plan.

The first major document reviewed included : **"Waste Form Qualification Report: WVDP Stabilized Sludge Wash Cement-Waste with Type V Portland Cement," Rev. 1, August 13, 1993, WVNS-TR-70-023. Prepared by W. J. Dalton.** This document will be referred to as the Qualification Report (Rev. 1), or the QR1. It summarizes the treatment of the sludge wash liquids, and their characteristics. The Qualification Report describes the recipes developed for solidification in Portland Type V cement, and the tests conducted to show that the process will produce a stable waste form in accordance with 10 CFR Part 61 and Appendix A to Rev. 1 of the NRC Technical Position on Waste Form (Ref. 4). The Qualification Report (Rev. 1) was reviewed by the NRC in late 1993 and a request for additional information (RAI) was sent to WVNS at that time. WVNS responded formally in early 1994 (Ref. 7); the responses included commitments to revise QR1 and the Process Control Plan (PCP).

After developing what it considered an acceptable Portland V cement recipe, WVNS produced 21 drums of solidified waste. Several waste compositions were prepared to simulate expected process variations. Some of the full-scale drums represent later sludge washes, since they were "spiked" with sulfate, elevating the concentration to 11% of the total dissolved solids. Some of the drums had different concentrations of total dissolved solids to model variations in evaporator operations. After at least 90 days curing, cores were taken from the drums for testing. Test results are described and evaluated in Section 4 of this TER.

The second major document reviewed in detail included : **"Process Control Plan for Cement Solidification of Decontaminated Sludge Wash Liquid Using Portland Type V Cement," Rev. No. 2, August 9, 1993, WVNS-PCP-004 prepared by M. N. Baker.** The Process Control Plan (PCP) describes the process and systems used to produce the solidified sludge waste liquids. Specific details about waste composition limits and verification procedures of the final waste forms during production are also given. These are presented in Section 4.4.10.

A revised Qualification Report (Rev. 2, or QR2, also prepared by W. J. Dalton and dated July 29, 1994) was sent to NRC August 2, 1994 and Rev. 4 of the PCP (prepared by R. J. Lewandowski and dated July 27, 1994) were sent to the NRC August 2, 1994. This TER includes PCP Rev. 4 (also called PCP4 in this review), QR2, and the information provided in the responses to the RAI.

4. TECHNICAL EVALUATION

The following technical evaluation compares information provided in the Qualification Report (Rev. 2) and the Process Control Plan (Rev. 4) with the applicable regulatory requirements of 10 CFR Part 61 and the guidance in the 1991 Rev. 1 TP, Appendix A, on cement-solidified waste forms (Ref. 4). According to the Qualification Report (Rev. 2), WVNS intends to qualify <u>all</u> sludge wash wastes solidified with Portland Type V cement under the series of tests reviewed within this TER. This includes preliminary formulations containing a lower waste loading, and a second sludge wash. The second sludge wash is understood by the NRC staff to be the final one.

4.1 <u>Characterization of Waste Composition</u>

Appendix A to the January 1991 Rev. 1 TP describes waste characterization as including at least the following minimum information:

- identification of major constituents (e.g.,resin type, diatomaceous earth, crud) including primary ions/salts and other solids,
- density,
- pH,
- temperature,
- a check for the presence of secondary constituents that could significantly affect the hydration of the cement*, and
- radioisotopic analysis.

Discussions in Appendix A of the TP indicate that waste characterization should include quantitative information on the major constituents, namely, anticipated ranges of concentrations or percentage compositions, and anticipated ranges of the density (or specific gravity), pH, and temperature. Also, a solidification process should demonstrate a correlation between the waste formulations used to prepare the qualification test specimens and the actual wastes encountered in the field in terms of the characteristics listed above (with the exception of the radioisotopic

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*NRC Information Notice 90-31 (Ref. 8) and Table I of Appendix A to Rev. 1 TP list most such secondary constituents, but not necessarily all of them.

analysis, which is needed for waste classification purposes). Because a given type of waste stream will often differ in these characteristics from one nuclear facility to another and over the course of time at any one facility, it is impractical for waste processors in the commercial sector to perform qualification testing on every possible combination and concentration of minor constituents in that waste stream. Nor is it considered practical or necessary for a waste processor to perform a complete quantitative chemical analysis on every batch of waste that is produced. It is, however, necessary for waste generators and processors to be cognizant of the types of chemicals which may cause problems for cement solidification of radwaste so that contamination of the waste stream may be prevented, or the waste pre-treated, as appropriate, if the problem constituents are contained in the waste stream.

Waste characterization is summarized in Section 3 of QR2. WVNS does not expect the sludge wash liquids to exhibit the degree of variation encountered in commercial nuclear power plant waste. Table 1 summarizes these characteristics, which are derived from information contained in Tables 2 and 3 of the Qualification Report (Rev. 2). These tables show, for the most part, the composition of samples taken directly from Tank 8D2 during sludge wash #1 and #2, respectively, and describe the waste prior to ion-exchange (zeolite) processing and evaporation to a nominal 30 weight percent (wt%) total dissolved solids (TDS). Some of the constituent compositions reflect values for samples taken from holdup tanks after processing, but before solidification. The items evaluated are as follows:

Major constituents: The constituent concentrations shown in Table 1 for sludge wash #1 represent averages of samples taken during the processing and solidification campaign, from April, 1992 to May, 1994. Most samples of sludge wash #1 were obtained monthly from Tank 8D2. These were used for analysis of both major and minor constituents, according to Table 2 of QR2. Some constituents were measured after processing, when the concentrated liquids were stored in one of two holdup tanks or the waste dispensing vessel (WDV). Sludge wash #2 is characterized by fewer samples, because of a smaller volume of waste and a shorter solidification campaign. According to QR2, that campaign is still on-going.

The actual waste to be solidified is concentrated in an evaporator to total dissolved solids (TDS) concentration of 26 to 33 weight percent (wt%). The constituent composition, in terms of dry wt%, should not change because of the evaporator operation, and data to support this is presented in Table 6 of QR2. The potential ranges of composition for the chemical constituents were not shown in Rev. 1 of the QR, and WVNS committed to providing the expected ranges in its response to the RAI. Tables 2 and 3 of QR2 show standard deviations from averages calculated from multiple sample measurements. Standard deviations do not represent the range of constituents possible, since the mathematical formula used can understate the limits possible, particularly when the number of samples is large. Sludge wash #1 is characterized with a larger number of samples (16 maximum). It is notable that the sludge wash waste is probably more homogenous in chemical composition than most commercial LLW.

Table 1
Characteristics of Sludge Wash #1 and #2 Solutions[a]

Chemical Constituent	Sludge Wash #1[b]	Sludge Wash #2[c]
Major:		
Sodium (Na) (wt % solids)	32.34 ± 2.52	36.10
Nitrate (NO_3) (wt % solids)	25.03 ± 2.20	18.71
Nitrite (NO_2) (wt % solids)	25.52 ± 1.81	29.93
Sulfate (SO_4) (wt % solids)	9.64 ± 0.91	8.98
Minor:		
Aluminum (Al) (wt % solids)	0.15 ± 0.02	0.144
Chloride (Cl) (wt % solids)	0.27 ± 0.03	NR
Uranium (U) (wt % solids)	0.0023 ± 0.0008	NR
Hydroxide (OH) (molarity)	0.504[c]	0.753
TOC (wt % solids)	0.0235 ± 0.0026[c]	NR
TIC (wt % solids)	1.092 ± 0.23[c]	NA
Total Dissolved Solids (wt %)	17.24 ± 2.19	30.14 ± 0.28
Density (g/mL)	1.131 ± 0.020	1.241 ± 0.002
pH	12.36 ± 0.23	12.85 ± 0.06

a Data taken from Tables 2 and 3 of QR2. Not all minor constituents are shown. Values with no standard deviation are single sample measurements. NR = not reported.

b Average values during processing from April, 1992 to May, 1994. Samples were taken directly from Tank 8D2 unless otherwise noted.

c Samples taken from one of three holdup tanks (5D-15A1 or 5D-15A2 or WDV) after processing, but before solidification.

Changes in major constituent concentrations when the waste stream was changed from sludge wash #1 to wash #2 are relatively small, except for sodium (Na) and are not expected to impact on the solidification process, according to the QR2. For sludge wash #2, sodium content is higher by four wt% and the nitrate/nitrite ratio decreased from one to about 0.6. The increase in sodium is not matched by corresponding increases in sulfate, nitrate, or nitrite. This suggests that other minor constituent anions are dissolving from the sludge, and if these include phosphate, carbonate, or chloride, properties of the solidified waste, such as set time or ultimate compressive strength, may be affected. This difference between sludge wash #1 and #2 is discussed further in Section 4.4.9.

The total solids concentrations of major and minor constituents in Table 1 account for about 95.5 wt% for sludge wash #1, and 93.9 wt% in sludge wash #2. The presence of other dissolved constituents or experimental uncertainties in the measured values could account for the other 4.5 and 6.1 wt% solids, respectively, in the waste stream. The presence of unidentified minor constituents or deviations in the nominal compositions are of little concern unless they interfere with the solidification process.

Density: The density of the decontaminated sludge wash varies directly with wt% TDS, from 1.154 g/mL at 19 wt% TDS to 1.277 g/mL at 33 wt%.

pH: The pH of the concentrated decontaminated sludge washes is one of the waste variables controlled under the PCP. The minimum required value before solidification can proceed is 12.0.

Temperature: QR2 states that the temperature of the concentrated decontaminated sludge wash is ambient, which, for the cement solidification system is about 90°F.

Minor constituents: Table 1 shows six constituents with concentrations about equal to or less than 1.0 wt% of total solids. Organic constituents (total organic carbon, or TOC) are listed as 0.0235 ± 0.0026 wt%, and inorganic carbon (carbonate, or TIC) is present at 1.09 ± 0.23 wt% in sludge wash #1. TOC and TIC were not reported for sludge wash #2. The review by NRC's consultant, BNL, questioned the values for hydroxece (OH) which were reported as 0.50 and 0.75 molarity for wash #1 and #2, respectively. These OH concentrations would result in pH values of more than 13.5. In a teleconference on November 1, 1994, WVNS clarified the OH concentrations as representing total alkalinity derived from titrimetric analysis, which includes contributions from sulfate, carbonate, and phosphate.

Radioisotope analysis: As noted earlier, this review focussed on the chemical and physical characteristics of the waste stream, since the waste classification was not expected to vary, and because WVNS had committed to processing all liquid wastes from Tank 8D2 to a form that met 10CFR Part 61 stability requirements. However, the NRC staff request for additional information (RAI) in Question 2 questioned the radionuclide analysis presented in Tables 3 and 4 of the Qualification Report (Rev. 1). Values for potential ranges of radionuclide concentrations were requested, as well as the identities of the specific plutonium isotopes measured. In its response to the staff's RAI, WVNS committed to providing a "typical range for each key radionuclide in Table 3 based on processing though a new ion-exchange bed and a bed that has reached its capacity," and to clarify plutonium isotopes included in alpha-plutonium analyses. WVNS revised and combined the radionuclide analysis into Table 4 of QR2, as agreed.

The waste characterization data provided in QR2 appears to be complete. More data characterizing sludge wash #1 are reported, because that campaign is finished. These data represent the waste before processing. The limited data for sludge wash #2 characterize the waste after processing but before solidification. The qualification testing was conducted with samples prepared from actual full-scale waste forms that had been prepared from sludge wash #1. In its response to the RAI Question 1, WVNS committed to explicitly listing the chemical composition of decontaminated (after processing) sludge wash #1 concentrate and the anticipated range of each constituent for the remaining sludge washes. The revisions to the Qualification Report do not completely fulfill this commitment, because the data for sludge wash #1 for the most part reflect analyses done on sludge wash before processing. However, the characterization is sufficient in that the zeolite processing followed by evaporation is not expected to change constituent concentrations expressed as a percentage of total dissolved solids.

It is worth mentioning that, in QR2, the process limits were explicitly stated to include a range of 19 wt% TDS to 32 wt% TDS for sludge wash #1. However, qualification testing to demonstrate stability was confined to a lower waste composition limit of 26 wt% TDS for sludge wash #1. No TP qualification tests with sludge wash #2 (actual or simulated) were conducted. This point is discussed in more detail in Section 4.4.9.

4.2 Minimum Requirements of 10 CFR 61.56(a)

Section 61.56(a) of 10 CFR Part 61 specifies minimum requirements for all classes of waste. These requirements are intended to facilitate handling at the disposal site and provide for the protection of health and for the safety of personnel at the disposal site.

4.2.1 Packaging

Section 61.56(a)(1) of 10 CFR Part 61 specifies that waste must not be packaged for disposal in cardboard or fiberboard boxes. At West Valley the waste form is contained in steel drums or liners and thus satisfies this requirement.

4.2.2 Liquid Waste

Section 61.56(a)(2) of 10 CFR Part 61 specifies that liquid waste must be solidified or packaged in sufficient absorbent material to absorb twice the volume of the liquid. The decontaminated sludge wash is solidified and, therefore, fulfills this requirement.

4.2.3 Free Liquid

Section 61.56(a)(3) of 10 CFR Part 61 specifies that free standing liquid in the solid waste shall not exceed 1% of the volume of the solid waste. Section 4.4.7 below describes how this requirement is met.

4.2.4 Reactivity of Product

Section 61.56(a)(4) of 10 CFR Part 61 specifies that the waste must not be readily capable of detonation or of explosive decomposition or reaction at normal pressures and temperatures, or of explosive reaction with water. The cement-solidified decontaminated sludge wash is not capable of such reactions and thus satisfies this requirement.

4.2.5 Gas Generation

Section 61.56(a)(5) of 10 CFR Part 61 specifies that 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. The solidified waste forms satisfy this requirement.

4.2.6 Pyrophoricity

Section 61.56(a)(6) of 10 CFR Part 61 specifies that the waste must not be pyrophoric or contain materials which are pyrophoric. Pyrophoric liquid or solid are defined in Section 61.2. The solidified waste satisfies this requirement.

4.2.7 Gaseous Wastes

This provision (10 CFR 61.56(a)(7)) is not applicable to the subject waste forms.

4.2.8 Hazardous Waste

Under the Resource Conservation and Recovery Act (RCRA), the U.S. Environmental Protection Agency (EPA) has jurisdiction over the management of solid hazardous wastes with the exception of source, byproduct, and special nuclear material, which are regulated by the NRC under the Atomic Energy Act. Low-level radioactive wastes (LLW) contain source, byproduct, or special nuclear materials, but they may also contain chemical constituents which are hazardous under EPA regulations promulgated under Subtitle C of RCRA. Such wastes are commonly referred to as mixed low-level radioactive and hazardous waste (mixed waste).

Applicable NRC regulations control the byproduct, source, and special nuclear material components of the mixed LLW (10 CFR Parts 30, 40, 61, and 70); EPA regulations control the hazardous component of the mixed LLW (40 CFR Parts 260-266, 268 and 270). Thus, all of the individual constituents of mixed LLW are subject to either NRC or EPA regulations. However, when the components are combined to become mixed LLW, neither agency has exclusive jurisdiction under current Federal law. This has resulted in dual regulation of mixed LLW, wherein NRC regulates the radioactive component and EPA regulates the hazardous component of the same waste.

Under Section 10 CFR 61.56(a)(8), waste containing hazardous, biological, pathogenic, or infectious material must be treated to reduce to the maximum extent practicable the potential hazard from the non-radiological materials. The waste form consisting of the cement binder material plus the waste streams described in Section 4.1 of this evaluation does not contain biological, pathogenic or infectious material, and thus satisfies these requirements of 10 CFR Part 61.

This review does not evaluate EPA requirements relating to hazardous solid waste. The QR states that the waste liquids contain chromium in concentrations that classify the liquids as hazardous. However, TCLP testing of the solidified waste product shows that the final waste form is not hazardous under EPA test methods.

4.3 Stability Requirements of 10 CFR 61.56(b)

The requirements of 10 CFR 61.56(b) are intended to provide stability of the waste. Stability is intended to ensure that the waste does not structurally degrade and affect overall stability of the site through slumping, collapse, or other failure of the disposal unit and thereby lead to water infiltration. Stability is also a factor in limiting exposure to an inadvertent intruder, since it provides a recognizable and nondispersable waste.

4.3.1 Structural Stability

According to 10 CFR 61.56(b) and 61.7(b)(2), Class B and C waste forms must maintain their physical dimensions and form for 300 years under the expected disposal conditions such as weight of overburden and compaction equipment, the presence of moisture and microbial activity, and internal factors such as radiation effects and chemical changes. The solidified sludge waste product will be packaged in suitable containers, but the containers will be given no credit for stability. The evaluation for structural stability is discussed in Section 4.4 under recommendations of the 1991 Technical Position on Waste Form.

4.3.2 Free Liquid

Section 10 CFR 61.56 (b) (2) requires that wastes processed to a stable form have a liquid content that does not exceed 0.5 percent of the volume of the waste. The TP in Reference 4 Appendix A addresses this requirement. See Section 4.4.7, below.

4.3.3 Void Spaces

Section 61.56(b)(3) of 10 CFR Part 61 states that void spaces within the waste and between the waste and its package must be reduced to the extent practicable. At West Valley, containers holding the processed waste form are to be filled while the waste form is still fluid. Solidification then takes place in the container, thereby reducing the void spaces between the waste and the container to the extent practicable. The PCP specifies a minimum filling of drums of 85% during routine processing, which fulfills the requirement.

4.4 Recommendations of the Technical Position on Waste Form

The 1991 Technical Position on Waste Form (Ref. 4) recommends tests and criteria for demonstrating the stability called for in 10 CFR Section 61.56.

Stable low-level radioactive wastes are required to maintain their gross physical properties and physical identity for 300 years or more. Structural stability may be demonstrated by subjecting samples of the waste forms to a series of tests. The recommended tests include compressive strength, leach resistance, and resistance to biological attack, irradiation, thermal cycling, immersion in water, and correlation of lab-scale results with full-scale products, as demonstrated by compressive strength tests following these test exposures.

WVNS selected five drums from the 21 prepared with concentrated decontaminated sludge wash #1 for its qualification test program. Four of these had been "spiked" with sodium sulfate, one had not. Data describing the qualification test drums were listed in QR1 Table 7. The QR described expected process limits for its solidification process, but did not explicitly correlate these limits with the samples prepared for qualification testing. The staff's RAI (Question 6) requested a table clarifying this correlation, and WVNS committed to preparing such a table in its response. In QR2, a new Table 7 was added summarizing the chemical composition of the sludge wash (#1) used to make the 21 test drums. Table 7 of QR1 was re-numbered Table 8. In QR2, Section 6.3 was expanded to list the parameters varied in order to establish process limits. The parameters and value ranges covered by the 21 drums were:

* TDS: 19.9 wt% to 33.1 wt%,
* water to cement ratio: 0.45 to 0.60, and
* sulfate: 10.05 to 11.04 wt% solids.

The compositional ranges and compressive strength test results for the five selected test drums are presented in Table 2. Total dissolved solids in the waste liquids ranged from 26.1 wt% to

33.1 wt%, while water/cement ratios ranged from 0.49 to 0.55. Sets of cores from the drums were used for TP qualification testing. Note that the range of compositions tested, in terms of wt% TDS and water/cement ratio, does not encompass the full range of compostions for which qualification is requested nor the range of compositions available for testing. The WVNS response to Question 6 of the RAI on this difference was considered inadequate and has resulted in a commitment from DOE to perform verification testing as described in Section 5.

The following sections summarize the qualification testing of the cement-solidified decontaminated sludge wash #1 waste forms as described in the Qualification Report (Rev. 2). Test results are evaluated against the criteria recommended in Appendix A of the 1991 TP.

Table 2
Compositional Process Limits and
Compressive Strength Test Results

Drum No.	84934	83552	83212	84894	83760
TDS (Wt%)	26.10	28.80	29.94	29.94	33.10
Sulfate (Wt% Dry Salts)	11	10	11	11	11
Water/Cement Ratio	0.50	0.55	0.52	0.52	0.49
Compressive Strength Test Results (psi)					
Baseline	1680 ±450	800 ±140	1160 ±160	1400 ±210	1130 ±260
After 90-day immersion	2140[a] ±450	1170 ±160	1790[b]	1700[a] ±570	1450[a] ±760
After thermal cycle	NT[c]	NT	NT	2200 ±190	NT

a: Two samples only b: One sample only c: NT = not tested

4.4.1 Compressive Strength

In Appendix A to the TP (Ref. 4), NRC specifies a compressive strength of 500 psi mean compressive strength for waste form specimens cured for a minimum of 28 days. In some cases 28 days may be inadequate for essentially complete curing of waste form specimens. Therefore, Appendix A recommends that sufficient specimens be prepared to determine the compressive strength increase with time to ensure that the specimens have attained near-maximum compressive strength. The specimens tested using ASTM C39 procedures (Ref. 9) should be right circular cylinders 2 to 3 inches in diameter with length approximately twice the diameter. Because of the scatter inherent to compressive strength data for a brittle material such as cement, Appendix A specifies a minimum of ten specimens when determining the compressive strength.

Compressive strengths of 30 cylindrical core specimens obtained from top, middle and bottom locations in five waste drums were measured following ASTM C39. Six cores from each drum were tested. WVNS is claiming the nominal 30 wt% TDS waste is its "average" waste and tested two drums (12 core samples) at this composition. Baseline compressive strength does not appear to correlate with TDS levels or water-cement ratio, and exhibits considerable scatter. Drum average strengths ranged up to a high maximum strength of 1680 psi. The lowest average measured compressive strength was 800 ($\pm$140) psi for the 28.8 wt% TDS composition. Interestingly enough, this composition is the only one without sulfate added.

The issue of maximum strength of the waste form was raised in the RAI, since QR1 contained statements that the compressive strength was still increasing after 90 days curing time. Test results of strengths for the 30 wt% TDS at different times, ranging from 93 days to 120 days were listed in QR Table 8. However, the same strength data had been averaged to provide a compressive strength value for the 30 wt% TDS recipe. In its response to the RAI, WVNS agreed that the maximum strength would be better resolved with a long term surveillance test program, and committed to developing and initiating a program. This program was submitted to NRC (Ref. 10), and is discussed in Section 4.4.10.2.

Another issue raised in the staff's RAI concerned the process parameters and how these affected compressive strength in the waste form. WVNS responded that the effects of process parameters on compressive strength were discussed in Section 7.10.1 of the QR, and committed to expanding that discussion further to clarify the issue. Revisions in QR2 Section 7.10.1 adequately address these concerns, and are discussed in Section 4.4.10.1 of this TER.

All compositions tested had compressive strengths well in excess of the minimum 500 psi criterion called for in Appendix A to the TP (Ref. 4).

4.4.2 Radiation Resistance

Appendix A to the TP (Ref. 4) recommends that specimens of proposed waste forms containing ion-exchange resins or other organic materials should remain stable after exposure to an absorbed gamma ray dose of 10^8 rad. Irradiation testing need not be conducted on waste forms containing inorganic materials unless the expected cumulative dose for the corresponding actual waste forms is expected to exceed 10^9 rad. The irradiated cement waste form specimens should have a minimum compressive strength of 500 psi when tested in accord with ASTM C39 (Ref. 9) There should be no visual evidence of significant degradation of the specimen, e.g., no cracking or spalling, after the exposure to radiation.

The decontaminated sludge wash does not contain ion-exchange media and the total organic carbon content is about 0.02 wt%, according to Table 2 of QR2. Furthermore, WVNS states that the total dose to the waste form will be less than 10^9 rad. For such low organic carbon content and total dose to the waste form, the irradiation test is not required.

4.4.3 Biodegradation Resistance

Appendix A to the TP (Ref. 4) recommends that waste form specimens for waste streams containing carbonaceous materials be tested for resistance to biodegradation in accordance with both ASTM G21 (Ref. 11) and ASTM G22 (Ref. 12). These are tests for resistance of synthetic polymeric materials to degradation by fungi and by bacteria, respectively. No indication of culture growth should be visible. Following biodegradation testing, cement waste form specimens should have compressive strengths greater than 500 psi as tested using ASTM C39. There should be no visual evidence of significant degradation of the specimen, e.g., no cracking or spalling, after the biodegradation testing.

During a meeting with NRC staff held at West Valley on December 19, 1990, it was concluded that since the decontaminated sludge wash cement waste form contains no ion-exchange resins or oils and its total organic carbon content is less than 500 ppm, biodegradation testing is not necessary.

4.4.4 Leachability

The 1991 TP recommends that leach testing of cement-stabilized wastes be performed for 5 days in accordance with the procedure described in ANSI/ANS-16.1 (Ref. 13). In addition to the demineralized water specified in ANSI/ANS-16.1, Appendix A to the TP specifies that the specimens should also be exposed to a synthesized sea water leachant. The bulk of the leach testing should be performed with whichever of the two leachants is found to be more aggressive. An acceptable method of identifying the more aggressive of the two leachants is to perform 24-h (or longer) leaching measurements on both leachants in order to determine which leachant results in a lower leach index (i.e., a higher leach rate.) The leachability index, as calculated in accordance with ANSI/ANS-16.1, should be greater than 6.0.

Three one-inch by three-inch cylindrical cores from drum #84894 (30 wt%TDS) were tested for leach resistance in both demineralized water and synthetic seawater. Analysis of the leach solution focussed on four radionuclides: Sr-90, Tc-99, Cs-137, and α-emitting plutonium isotopes (α-Pu in the QR). The reported leach indices are all greater than 6. Individual leach indices are shown in Table 3.

Table 3
Leach Indices for Portland V Cement and Sludge Wash Waste Form

Radionuclide	Demineralized Water	Synthetic Seawater
Tc-99	8.3 ± 0.3	8.3 ± 0.4
Sr-90	9.6 ± 0.7	9.8 ± 0.7
Cs-137	8.1 ± 0.3	8.1 ± 0.3
α-Pu	9.6 ± 0.9	10.4 ± 0.6

There appear to be no significant differences in leach indices for the two leach solutions. Thus, neither demineralized water nor synthetic seawater can be considered more aggressive. The lowest leach index is 8.1 for Cs-137. The 30 wt% solidified sludge wash exceeds the TP leach index criterion. Although the full range of waste form compositions was not tested, it is reasonable to conclude that the solidification process will produce waste forms with similar leach resistance.

4.4.5 Immersion Resistance

Appendix A to the TP recommends that, following immersion in water for at least 90 days, waste specimens should maintain a minimum compressive strength of 500 psi as tested using ASTM C39. The water used should be the more aggressive of the two leachants identified during leach testing. The compressive strength after immersion should be at least 75 percent of the compressive strength measured before immersion. There should be no visual evidence of significant degradation, such as cracking or spalling, of the specimen after the 90-day immersion period. Certain waste streams, containing bead resins, chelates, filter sludges, and floor drain wastes, can exhibit complex relationships between cure time and immersion resistance. For these Appendix A recommends additional immersion testing on specimens that have been cured in sealed containers for at least 180 days. This additional testing consists of at least 7 days immersion followed by 7 days drying in ambient air at a minimum temperature of 20°C. After drying, the specimens should meet the post-immersion compressive strength and visual criteria specified above.

From previous leach testing with laboratory scale specimens, WVNS had concluded that synthetic seawater was the more aggressive leachant. Three cylindrical core samples from each of the five drums selected for the qualification test program were immersed in the seawater for 90 days. Average results are summarized in Table 2. Five of the fifteen samples could not be tested for compressive strength after immersion because they were cracked sufficiently or split and therefore unacceptable for testing per ASTM C39 specifications. Three of the cracked samples were from the two drums prepared at the composition midpoint of 30 wt% TDS sludge wash.

The cracking was said to be due to the coring operation, which on full-scale drums is extremely difficult. This explanation was questioned in the RAI. Samples are prepared by using a coring drill, penetrating the waste form for six to eight inches, with a minimum of water. After coring to the appropriate depth, the tool is withdrawn and the core is broken off by insertion of a wedge into the gap around the core. Samples removed in this manner often have cracks as well as an irregular surface at the fracture face. The specimens have the irregular surfaces sawed off to complete the cylindrical shape. Since the specimens are cut dry or nearly so, observation of cracks is difficult.

All the core samples tested after immersion showed an increase in compressive strength compared to the baseline samples. Thus, the composition limits tested surpass the TP criterion because they exceed 75% of the baseline compressive strength. One issue to be resolved is that of some samples cracking. Although the WVNS explanation seems reasonable, it cannot be confirmed without additional testing. WVNS is addressing the issue by including immersion tests in the long term test program.

4.4.6 Thermal Cycling

Appendix A to the 1991 Rev. 1 TP recommends that thermal cycling tests be conducted in heating and cooling chambers conforming to those described in ASTM B553 (Ref.14). Thirty thermal cycles between 60°C and -40°C should be carried out, but in a manner which allows the specimens to come to thermal equilibrium at the high and low temperature limits. There should be no visual evidence of significant degradation of the specimen, e.g., no cracking or spalling, after the thermal cycling. Following testing, the specimens should have compressive strengths greater than 500 psi as tested using ASTM C39.

Three core samples from drum #84894 (30 wt%TDS) were tested according to the recommended ASTM procedure. Average results are shown in Table 2. The criterion of a minimum 500-psi compressive strength after thermal cycling was exceeded.

4.4.7 Free Liquids

Appendix A to the 1991 TP recommends that waste specimens have less than 0.5 percent by volume of the waste specimen as free liquids as measured using the method described in ANS 55.1 (Ref. 15). Free liquids should have a minimum pH of 9, which is considered representative of the alkaline properties of cement.

The Qualification Report describes two alternative methods used to detect free liquids. Small-scale cubes, similar to those prepared under the Process Control Plan, were made and examined for free liquid (designated "bleed water" in the QR). The cubes made covered the range of waste form compositions covered in the qualification test program. No signs of free liquid were seen. The second method was the coring operation used to obtain samples for the qualification test program. It was noted that no free liquids were observed in the five full-scale drums which were cored.

These methods show that the solidification process meets the free liquid criterion of the TP.

4.4.8 Full-Scale Specimen Test Results

Appendix A to the 1991 TP (Ref. 4) recommends that test data from sections or cores of the anticipated full-scale products should be obtained if small, simulated laboratory-size specimens are used for the TP qualification testing. Full-scale test data are to be used to demonstrate that the characteristics of actual size products correlate with those of simulated laboratory-size specimens. Non-radioactive full-scale specimens can be used, but they should be fabricated using actual or comparable solidification equipment. The correlation should be established by performing (1) compressive strength tests on material cured for at least 28 days, and (2) 90-day immersion followed by compressive strength tests for the waste that is most difficult to solidify. Appendix A also recommends that samples from full-scale specimens should be destructively analyzed to ensure that the product is homogeneous to the extent that all regions of the product can expect to have compressive strengths of at least 500 psi.

The entire TP qualification test program used cores from five full-scale drums after cure times of at least 90 days. The full-scale specimens had been processed in the Cement Solidification System from actual sludge wash liquids (although some had added sulfate). Nine of the 21 drums prepared for the qualification test program were monitored for temperature changes during curing. The top and central portions of the drum always reached higher temperatures than the bottom portions (85°C vs. 60°C). The core samples for the test program were obtained from top, middle and bottom locations in the drums, and showed no significant differences in compressive strength attributable to location. All compressive strengths were well above 500 psi. Thus the TP criterion for full-scale specimen tests to confirm processed waste homogeneity was met and exceeded.

4.4.9 Qualification Test Specimen Preparation

Appendix A to the 1991 Rev. 1 TP recommends that certain precautions be taken regarding the ingredients, mixing, curing and storage of qualification test specimens as follows:

> Ingredients - The surrogate wastes used for qualification testing should simulate the actual wastes intended to be stabilized with the binder material under consideration. For example, the characterization parameters used to characterize the actual waste, namely, major constituents, density or specific gravity, pH, temperature, and minor ingredients, should, for the surrogate wastes, bracket or envelope those of the corresponding actual

waste to the extent practicable, and where differences exist, the potential significance of such differences should be discussed.

Mixing - In preparing laboratory-sized qualification test specimens, it should be shown by analysis and/or testing that the type of equipment used, the mixing time, the speed of the mixer, etc., will, in combination, impart the same degree of mixing to the laboratory specimens as the full-scale mixing equipment will impart to full-scale waste forms, and that the degree of mixing is sufficient to ensure production of homogeneous waste forms.

Curing - (1) To ensure that the laboratory specimens endure curing conditions reasonably similar to those of the full-size products, the waste-form centerline temperature profile as a function of time should be obtained for the largest full-sized waste form to be qualified for each waste stream. That profile should be duplicated to the extent practical in the laboratory specimens, for example, by oven curing for a time period equivalent to the peak heat of hydration period. (2) Care is needed in formulation to preclude temperatures at or above the boiling point of the pre-solidification mix. (3) Sufficient test specimens should be prepared to determine the compressive strength increase with time in order to ensure that the qualification testing is performed on essentially cured specimens as evidenced by a compressive strength greater than 75% of the projected peak compressive strength.

Storage - In order to simulate the environment within a typical full-scale waste form liner and to prevent loss of water which might affect the performance of specimens during subsequent testing, the qualification test specimens should be kept in sealed containers during curing and storage prior to testing.

WVNS conducted its qualification test program using specimens prepared under full-scale production conditions with actual wastes. This meets the criteria of concern in this section, subject to the following caveat. The composition of the sludge wash #1 liquids was varied from 26 wt% to 33 wt% TDS, and in addition, sodium sulfate was added to simulate the expected change in composition for subsequent sludge wash operations. The proposed limits for the process in terms of the waste chemical composition, was not clearly tabulated. A clearer definition of the chemical composition limits expected was called for in the RAI, and WVNS committed to revising the Qualification Report to show process limits more clearly. Rev. 2 of the Qualification Report states that the test program is intended to qualify sludge wash #1 wastes concentrated to 20 wt% TDS up to 33 wt% and sludge wash #2 wastes, as well.

Since no qualification tests were conducted using simulated or actual sludge wash #2 wastes or with sludge wash #1 concentrated to 20 wt% TDS, there is some question as to the applicability of the results of the test program to these wastes. They represent significant process deviations which do no correspond to "the actual wastes intended to be stabilized with the binder material under consideration."

The test program covered waste compositions ranging from 26 wt% TDS to 33 wt% TDS. The PCP recipes range from 19 wt% TDS to 33 wt%TDS. In QR2, WVNS states that the wastes solidified with less than 26 wt% TDS were part of the process to increment system operations from the previous Portland Type I cement recipe that had been used. WVNS position is that the 19 to 26 wt% TDS solidified wash #1 wastes are acceptable because:

a) the recipe used is identical to that developed for Portland Type I cement, which was qualified according to TP guidelines,
b) lower wt% TDS does not adversely affect waste form stability, and
c) 2-inch verification cubes produced using sludge wash #1 at 20 wt% TDS had an average compressive strength above the recommended 500 psi minimum recommended in the TP.

The first two items are questionable because the effects of minor constituents on portland cement set times and strength development are not easily predicted. It is recognized (Ref. 16) that several salts, as single additives to portland cement used in construction, can have both accelerating and retarding effects on cement set times and hardening, depending on their concentration. The "effect produced often varies with the composition of the Portland cement used." (Ref. 16, p. 301) Combining agents that act as retarders or accelerators or both to produce certain set and strength properties will not necessarily apply to other Portland cement compositions. The 2-inch verification cubes (item c) may demonstrate that set times are acceptable for the solidification process, but strength development and long-term durability have not been demonstrated for the 20 wt% TDS formulation. Similar arguments apply to sludge wash #2, which, although it will be processed within the tested TDS range, has a different proportion of major constituents and unidentified minor constituents.

Some degree of testing should be conducted on the "incremental" recipes, i.e., waste products made with less than 26 wt% TDS, and on products made from sludge wash #2. The testing should include compressive strength measurements and immersion tests followed by compressive strength tests. As described in Section 5, DOE has committed to perform this testing in its long term program.

4.4.10 Process Control Plan

A Process Control Plan was prepared by WVNS for controlling waste form production. In addition to providing the PCP for review, WVNS included in its Qualification Report a discussion of Applicable TP criteria.

4.4.10.1 Process Parameters

According to Appendix A to the 1991 Rev. 1 TP, for each LLW formulation, the generic PCP should identify and restrict within acceptable bounds the following variables which influence the process and affect the product:

* Type of waste, for instance, bead resin, powdered resins, boric acid, sludges;

* Waste characteristics which affect solidified waste properties, such as pH, oil content, chelating agents, water content, minor constituent concentration limits;

* Solidification binder components and additives, e.g., type of cement, water, lime, silica fume, fly ash, furnace slag, and their order of addition; and

* Physical process parameters, e.g., maximum temperature, mixing equipment required, mixing speed and curing times.

Appendix A to the TP also specifies that the PCP provide certain other process information:

* How representative samples of the feed waste are to be obtained for preparing PCP verification and surveillance specimens;

* Typical and maximum batch sizes;

* The number of PCP specimens to be taken for each batch; and

* Where and how out-of specification process parameters are dealt with.

The WVNS PCP lists two sets of items for controlling the process. The first set, identified as product requirements, is necessary for producing an acceptable waste form. Product requirements are:

* water/cement ratio,
* TDS (wt%) of sludge wash solution,
* sulfate concentration in sludge wash solution,
* sludge wash solution pH,
* drum percent volume filled,
* free water in drum, and
* verification sample compressive strength.

Process requirements are necessary for smooth operation of the Cement Solidification System, and include:

* mix time,
* recipe additive additions,
* gel time of verification sample, and
* automatic data base updates.

If there are upsets in either set of requirements, the suspect drum is set aside for further evaluation. Product requirement upset evaluations will include compressive strength tests and leachability tests. Process requirement upsets will involve a technical evaluation to determine product acceptability.

The Cement Solidification System processes waste in approximate 5,000 gallon batches. Waste is tested for density (from which wt% TDS is calculated), pH, radionuclides, and sulfate concentration. The data from this analysis is used to choose a solidification recipe from the limited set available. The recipe is chosen based on the TDS wt% value. A complete set of recipes is shown in Tables A1-1 to A1-7 in the PCP. When the recipe is chosen, a verification specimen is prepared and observed for gel time, and after 24 hours, crushed for compressive strength measurements. Full-scale solidification of the 5,000 gal batch is initiated only if the compressive strength of the verification sample is within specification for that recipe.

Specification of the process parameters is given in the PCP, as called for in the TP Appendix A, and in this respect the PCP meets applicable TP criteria. However, the recipe range allowed in the PCP exceeds that encompassed by the qualification test program. This difference is discussed in Section 5.

4.4.10.2 Verification and Surveillance Specimens

According to Appendix A of the TP, verification specimens should be prepared prior to a particular waste solidification campaign at a licensed facility. Actual waste should be solidified using the recipe qualified in laboratory testing for that waste stream. Mixing conditions of the waste with the cement and additives should duplicate to the extent practical full-scale mixing. Verification specimens should be cured under conditions (especially temperature-time profiles and relative humidity) similar to those used in the laboratory qualification test program. These short-term (24-hour) PCP verification specimens should be free of significant visible defects, exhibit less than 0.5% free liquid by volume. Within 24 hours after preparation, PCP specimens should exhibit a compressive strength within two standard deviations of the mean compressive strength obtained at 24 hours for test specimens from the associated laboratory qualification test program for the waste formulation. Compressive strength may be determined by ASTM C39 or by an alternative penetrometer method as described in Appendix A. For certain "problem" waste streams (in particular, bead resins, chelates, filter sludges, and floor drain wastes), sufficient PCP specimens should be prepared to permit the retention, examination and testing of surveillance specimens as described in Appendix A.

The PCP developed for the solidification of sludge wash using Type V Portland cement gives procedures for the preparation of verification specimens, but not surveillance specimens. The sludge wash waste is not one of the "problem" waste streams explicitly cited in TP Appendix A as requiring a surveillance program. However, WVNS has committed to a long-term monitoring and compressive strength test program for the sludge wash. The long term surveillance program was submitted to NRC in March of 1994 and found to conform to or conservatively exceed the recommendations of the TP guidelines (Ref. 17).

The verification specimens are 2-inch cubes which are observed for gel time, set time and free liquid. After 24 hours, the cube is tested for compressive strength. Although the cubes are not recommended in the TP for compressive strength testing, they are an acceptable geometry since WVNS developed a significant data base of strength measurements at 24 hours cure time correlating cube strength with qualification test sample compressive strength. Data for these correlations for waste compositions from 19 wt% to 33 wt% TDS are shown in the Qualification Report, Rev. 2, Tables 13 to 16. The strength of the verification cubes at 24 hours is lower than that for the qualification cylindrical core samples, but the core samples had been cured for more than 90 days.

Five questions in the staff's review were relevant to the acceptability of the procedures for verification samples described in the QR and PCP. The first of these (Question 19) referred to verification specimen data summarized in QR2 Tables 13 to 16. Slurry densities are tabulated and show unexpected variations for identical compositions. WVNS explained the variations adequately and stated that it would assess procedural changes to improve the accuracy of the measurement. Because the waste liquid and cement slurry density is not a crucial process parameter, no further action is required on this issue.

A second question (21) was concerned with the methodology used to calculate the minimum compressive strength for process recipe acceptability. Gel time for acceptable verification samples must be greater than one minute, yet compressive strength values of some samples (20 wt% TDS composition, Table 12 in the QR) whose gel times were equal to one minute were included in the calculation of average compressive strength. Thus, the minimum acceptable compressive strength, using all sample values, was 290 psi. A minimum acceptable value calculated using only samples whose gel time is greater than one minute is 417 psi. WVNS in its response admitted that the measurement of gel time was "subjective." In QR2, WVNS apparently changed its methodology for defining "minimum process control compressive strength" for the laboratory cubes. Table 13 in QR2 (formerly Table 12 in Rev. 1) and the text were changed to show that the acceptable minimum strength was 505 psi. This was calculated from an average strength of 771 $\pm$ 133 psi for four cubes whose water to cement ratio was 0.62. This value includes samples whose gel time is equal to one minute. Gel time is considered an important process parameter, and the requirement described for the verification cubes in Table 20 of QR2 is "1 minute general minimum and 60 minutes maximum." The WVNS response to Question 21 is acceptable.

Staff RAI (Question 27) requested clarification of a PCP procedure (ACM-2401) that is used to measure total dissolved solids content in the sludge wash liquids when making verification samples. WVNS has added this to the PCP reference section, as promised.

Two RAI questions (30 and 32) dealt with radionuclide analyses and acceptance criteria for the sludge wash liquids. Radiological analyses for verification purposes are limited, and a full set of radionuclides present is calculated from correlations (ratios) established from earlier analyses. Question 30 asked for evidence that the ratios had not changed for the sludge wash liquids, and, in PCP4, WVNS updated the PCP to reflect a 1993 radiological analysis. Staff RAI (Question

32) pointed out an error in PCP Figure 7, in which it was stated that "there are no maximum values for cesium and strontium" for 10 CFR 61 Class C limits. WVNS revised the PCP and the SOP 00-13 Attachment that is illustrated in Figure 7 to correct the error.

The PCP (Rev. 4) conforms to the recommendations of TP Appendix A for preparing verification specimens to demonstrate control of waste processing. Sufficient data are presented to show that the 2-inch cube compressive strengths have been correlated to full-scale waste form strengths.

As noted earlier, WVNS has committed to a long-term test program that will provide surveillance specimens and to testing them. WVNS submitted its test plan (Ref. 10) to NRC, and the test plan was found to fulfill the recommended test approach for surveillance specimens found in the TP Appendix A (Ref. 16). The test plans involve saving several drums of sludge wash #1 solidified in Portland Cement Type V, and coring them for compressive strength specimens and immersion test specimens. Two issues were raised in NRC's review of the test plan related to the acceptability of sludge wash #1 wastes when concentrated to less than 26 wt% TDS, and the equivalence of Type V cement-solidified sludge wash #2 in comparison to qualified sludge wash #1 wastes. These issues have been resolved with the commitment of DOE to perform testing in the long term program, as subsequently described.

5. CONCLUSIONS

Overall, the review of the Qualification Report (Rev. 2) and Process Control Plan (Rev. 4) indicates that decontaminated sludge wash #1 concentrated to 26 to 33 wt% TDS and solidified with Portland Type V cement can meet, and in many instances exceed, the stability requirements of 10 CFR Part 61. However, two issues have been identified in NRC's review as items requiring resolution. These issues include the staff's concern for the cracking or splitting of five (out of fifteen) of the specimens during immersion testing, and the deviation from the waste composition limits that were qualified in the QR and PCP reports.

The cracking or splitting of some cores of the solidified waste during immersion testing was explained by DOE as resulting from the coring operations. Core drilling is conducted nearly dry, and core removal involves fracturing the core from the bulk waste form. WVNS thought that "hairline" cracks were present in the cores before immersion in these forms, and constituted an initiation point for eventual splitting during immersion. This explanation is plausible and is to be verified by WVNS in assessments to be made in the long term surveillance program.

Waste composition limits intended to be qualified were not clearly described in the initial report submittals. Later, in Rev. 2 of the Qualification Report, WVNS stated its intent to solidify sludge wash that was concentrated as low as 20 wt% TDS up to a limit of 33 wt% TDS. In addition, no qualification tests had been conducted using either simulated or actual sludge wash from decontaminated sludge wash #2. The concern of the NRC staff and its consultant is whether the qualification testing actually completed is sufficiently applicable to 1) encompass sludge wash to as low as 20 wt% TDS, since testing completed was not below 26 wt% TDS, and 2) cover sludge wash #2 because of differences in chemical composition with sludge wash #1. To resolve this concern the NRC staff sought and received a commitment from DOE (Ref. 18) to identify and secure one drum from the West Valley storage cell of solidified wash #1 having a concentration of approximately 20 wt% TDS, and one additional drum of the solidified sludge wash #2. These additional drums are to be included in DOE's long term test program for compression strength and immersion testing, to confirm that these solidified wastes also meet the waste form stability requirements of 10 CFR Part 61. Upon NRC's receipt of favorable test results that demonstrate these solidified wastes do fulfill the provisions of NRC's Technical Position on Waste Form, the concern for the applicability of the waste composition limits will be considered resolved.

Based on the information and favorable results that have been provided in the Qualification Report and Process Control Plan, the NRC staff concludes that there is reasonable assurance that the cement solidification of the decontaminated sludge wash using Type V Portland cement will meet the waste form stability requirements of 10 CFR Part 61 and fulfills or exceeds the provisions of NRC's Technical Position on Waste Form (Rev. 1). This conclusion is predicated on the expectation that the test results from the long term test program will continue to be acceptable, and will confirm the attainment of satisfactory compression strengths and stability performance of the cement solidified decontaminated sludge wash waste. It is the understanding of the NRC staff that DOE will keep the NRC fully informed of the results from the long term test program and provide, as a minimum, the results and evaluation on an annual basis until the program is completed.

6. REFERENCES

1. Waste Form Qualification Program for Solidification of Sludge Wash Liquid with Type V Portland Cement, West Valley Nuclear Service Company, Inc., for the U.S. Department of Energy, West Valley Demonstration Project, Volume 3, Issued June 24, 1993.

2. Technical Position on Waste Form, Rev.0, U.S. Nuclear Regulatory Commission, May 1983.

3. Workshop on Cement Stabilization of Low-Level Radioactive Waste, U.S. Nuclear Regulatory Commission and National Institute of Standards and Technology, NUREG/CR-0103, NISTIR 89-4178, October 1989.

4. Waste Form Technical Position, Rev. 1, U.S. Nuclear Regulatory Commission, January 24, 1991.

5. WVNS Experience with Cement Solidification of Decontaminated Spent Fuel Waste, C.W. McVay, J.R. Stimmel, and S. Marchetti, pp.41-56 in Workshop on Cement Stabilization of Low-Level Radioactive Waste, U.S. Nuclear Regulatory Commission and

National Institute of Standards and Technology, NUREG/CR-0103, NISTIR 89-4178, October 1989.

6. White Paper - Removal of Plutonium from West Valley High-Level Liquid Waste, L.A. Bray, F.T. Hara, and T.F. Kazmeirczak, Draft C., January 1991, attached to letter, February 4, 1991, from W.F.MacKellar, WVNS, to T.J. Rowland, West Valley Project Office, DOE.

7. Letter with Subject: WVDP Respond to NRC Request for Additional Information on Type V Portland Cement Waste Qualification Program, from T.J. Rowland (WVPO), to J.O. Thoma (NRC), February 3, 1994.

8. IN 90-31, "Update on Waste Form and High Integrity Container Topical Report Review Status, Identification of Problems with Cement Solidification, and Reporting of Mishaps," May 4, 1990.

9. Standard Test Method for Compressive Strength of Cylindrical Concrete Specimens, ASTM C39-84, American Society for Testing and Materials, 1985 Annual Book of ASTM Standards, Vol. 4.02.

10. Letter with Subject: Cement-Waste Qualification Notebook Updates to Volumes II and III, from T. J. Rowland (WVPO), to G. C. Comfort (NRC), March 30, 1994.

11. Standard Practice for Determining Resistance of Synthetic Polymeric Materials to Fungi, ASTM G21-70, American Society for Testing and Materials, 1981 Annual Book of ASTM Standards, Part 41.

12. Standard Practice for Determining Resistance of Plastics to Bacteria, ASTM G22-76, American Society for Testing and Materials, 1981 Annual Book of ASTM Standards, Part 41.

13. Measurement of the Leachability of Solidified Low-Level Radioactive Wastes by a Short-Term Procedure, ANSI/ANS-16.1 - 1986, American Nuclear Society, La Grange Park, IL (1986).

14. Standard Test Method for Thermal Cycling of Electroplated Plastics, ASTM B553-79, American Society for Testing and Materials, 1981 Annual Book of ASTM Standards, Part 9.

15. American National Standard for Solid Radioactive Waste Processing System for Light Water Cooled Reactor Plants, ANSI/ANS-55.1 - 1979, American Nuclear Society, La Grange Park, IL (1979).

16. F. M. Lea, The Chemistry of Cement and Concrete, 3rd ed., Chemical Publishing Co., New York, NY (1971).

17. Review of Long-term Test Programs for Cement Solidified Sludge Wash Wastes, Technical Letter Report," B. S. Bowerman, Brookhaven National Laboratory, August, 1994.

18. Letter with Subject: NRC Requested Additions to Sludge Wash Cement Waste Long-Term Test Program, from T. J. Rowland (WVPO), to G. C. Comfort (NRC), March 6, 1995.

ENCLOSURE 3

UNITED STATES
NUCLEAR REGULATORY COMMISSION
WASHINGTON, D.C. 20555-0001

Mr. Thomas P. Rowland, Director
West Valley Project Office
U.S. Department of Energy
P.O. Box 191
West Valley, NY 14171

SUBJECT: TRANSMITTAL OF TECHNICAL EVALUATION REPORTS FOR "WASTE FORM QUALIFICATION PROGRAM FOR CEMENT SOLIDIFICATION OF SLUDGE WASH LIQUID," FOR STABILIZATION IN TYPE I OR TYPE V PORTLAND CEMENT (TAC NO. L21412)

Dear Mr. Rowland:

Enclosed you will find two Technical Evaluation Reports (TERs) prepared by the U.S. Nuclear Regulatory Commission's Division of Waste Management, upon completion of their technical review of the information contained in the subject qualification program (QP) reports. Enclosure 1 deals with stabilization of PUREX sludge wash using Type I Portland cement, and Enclosure 2 deals with Type V Portland cement. The TERs provide NRC staff's evaluation of the ability of the described processes to create waste forms which meet the structural stability provisions of 10 CFR 61.56, and the relevant sections of the Branch Technical Position on Waste Form, Rev. 1 (TP). Although work performed by the Department of Energy (DOE) at West Valley is not subject to 10 CFR Part 61 regulations, DOE has voluntarily chosen to meet the waste characteristics and stability provisions of 10 CFR 61.56 and the associated TP guidance.

Based on the information and favorable results that have been provided by the QP, NRC staff concludes that there is reasonable assurance that the cement solidification of the decontaminated sludge wash with Type I or Type V Portland cement, using the recipes described in the respective Process Control Plans, will satisfy the waste form stability requirements of 10 CFR Part 61, and fulfills or exceeds the applicable provisions of the TP. Full concurrence with this determination is based upon resolution of minor issues which are identified in Section 5 of each TER. Also, NRC concurrence is predicated on the expectation that the results from the long term test programs will continue to be acceptable, and will confirm the attainment of satisfactory compressive strengths and stability performance of the cement solidified decontaminated sludge wash waste.

Notwithstanding the favorable findings given in the TERs, please note that the ultimate acceptability of the waste forms may be subject to the disposal restrictions and requirements established by operators and governing regulatory agencies other than NRC. Copies of the enclosed TERs will be forwarded to the State of New York and the NRC Office of State Programs for their information and use.

It is the understanding of NRC staff that DOE will keep NRC fully informed of the results from the long term test program and provide, as a minimum, the results and evaluation on an annual basis until the program is completed. NRC also requests that DOE inform us of results of any further testing or processing relevant to the TER findings. If you have any questions, please call me on (301) 415-8106. Please reference the above TAC No. in future correspondence related to this action.

Sincerely,

Gary C. Comfort, Jr.
Licensing Section 2
Licensing Branch
Division of Fuel Cycle Safety
and Safeguards
Office of Nuclear Material Safety
and Safeguards

Project M-32