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**CEMENT ENCAPSULATION
OF LOW-LEVEL WASTE LIQUIDS
FINAL REPORT**

Topical Report

By
M. N. Baker
H. M. Houston

January 1999

Work Performed Under Contract No. DE-AC24-81NE44139

Prepared by
West Valley Nuclear Services Co., Inc.
10282 Rock Springs Road
West Valley, NY 14171-9799

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Prepared for
U.S. Department of Energy
Assistant Secretary for Nuclear Energy

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ABSTRACT

Pretreatment of liquid high-level radioactive waste at the West Valley Demonstration Project (WVDP) was essential to ensuring the success of high-level waste (HLW) vitrification. By chemically separating the HLW from liquid waste, it was possible to achieve a significant reduction in the volume of HLW to be vitrified. In addition, pretreatment made it possible to remove sulfates, which posed several processing problems, from the HLW before vitrification took place.

Waste characterization and recipe formulation work was done to develop a basic recipe that could be used to solidify and stabilize decontaminated waste concentrates with Type I portland cement. The basic recipe was qualified according to methods and guidelines prescribed in the Branch Technical Position on Waste Form Qualification issued by the U.S. Nuclear Regulatory Commission (NRC), Office of Nuclear Material Safety and Safeguards in 1983. Full-scale testing of this recipe led to further modification and testing. These efforts resulted in the production of several test drums made under actual operating conditions. Core samples taken from these drums showed excellent results. Supplementary testing confirmed that the modified recipe, which varied less than 2 percent in elemental composition from the originally qualified recipe, produced a waste form that exhibited excellent compressive strength, thermal cycling resistance, and compressive strength following water immersion. This recipe was used to encapsulate decontaminated supernatant concentrates processed during the first phase of HLW pretreatment operations. Both short- and long-term test plans were prepared before the start of processing operations to demonstrate compliance with NRC criteria for low-level waste form stability.

Slight variations in the chemical composition of waste liquids were anticipated for the second phase of HLW pretreatment, sludge wash operations. This phase of HLW pretreatment involved dispersing sulfate salts present in the semi-solid sludge layer in Tank 8D-2 through liquid addition and mixing. Resulting liquids containing the sulfate salts could then be decontaminated, concentrated, and encapsulated as a qualified cement waste form. Expected variations in the chemical composition of the sludge wash liquid, combined with subtle changes in tank chemistry and updating of NRC waste form qualification guidelines presented several challenges for recipe qualification and testing needed for sludge wash processing. These challenges were successfully addressed during a thorough examination of the testing process. Close evaluation of the test results required a number of modifications that were used to produce a more stable waste form. Chief among these changes was the decision to use Type V portland cement as the primary binding agent in the recipe formulation.

EXECUTIVE SUMMARY

The West Valley Demonstration Project Act, Public Law 96-368, directed the United States Department of Energy (DOE) to carry out a high-level radioactive waste (HLW) management project at the Western New York Nuclear Service Center (WNYNSC), in West Valley, New York. The site is the location of the only commercial nuclear fuel reprocessing facility to have ever operated in the United States.

According to the Act, liquid HLW held in underground storage tanks at the site is required to be removed and solidified into a form suitable for long-term storage and transportation to a federal repository. At the beginning of the West Valley Demonstration Project (WVDP), two key decisions were made that determined how the HLW would be solidified.

The first decision made was to separate HLW chemically from the alkaline supernatant that had formed from adding sodium hydroxide to nitric-acid-based waste streams produced during original reprocessing operations. These wastes were held in the underground storage tank designated as 8D-2. After chemically separating HLW from the supernatant, the HLW would then be combined with the sludge layer that also had formed from caustic addition, and the resulting decontaminated supernatant would be processed into a suitable low-level waste (LLW) form. The next decision made was to solidify the combined HLW (i.e., separated HLW and sludge) into a borosilicate glass waste form. These processing decisions were based on chemical, radiochemical, and physical characterization of waste samples taken from Tank 8D-2.

Extensive testing was done at two locations to develop a cement recipe suitable for solidification of the decontaminated supernatant: the Westinghouse Research and Development Center in Pittsburgh, Pennsylvania, and the West Valley Nuclear Services, Co., Inc. Analytical and Process Chemistry Laboratory (A&PC Lab) in West Valley, New York. The initial recipe used Type I portland cement. All portland cement mortars are made up of mixtures of cement, lime, silica sand, and water. They can achieve compressive strength two orders of magnitude greater than minimum compressive strength requirements needed to resist deformation in LLW waste burial trenches. Although the initial recipe produced excellent short- and long-term results, waste form samples made before the start of sludge wash processing showed noticeable deterioration after 90-day immersion testing. A rigorous review of the testing program helped to identify the cause of this failure and successfully modify the recipe. Later cement formulations used Type V portland cement to achieve all necessary waste form requirements.

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1.0 INTRODUCTION

Successful waste solidification and stabilization are related to the characteristics of binding agents used to treat wastes. Portland cement has been used as a binding agent to solidify and stabilize nuclear waste since the 1950s because of its high strength, low permeability, and resistance to most chemicals.

Chemical and radiochemical analyses of samples taken from high-level waste (HLW) storage Tank 8D-2 suggested that the liquid supernatant in the tank could be decontaminated. It also showed that the resulting decontaminated salt solution could be mixed with a binding agent like portland cement to produce a low-level waste (LLW) form that would achieve U.S. Nuclear Regulatory Commission (NRC) stability criteria.

A detailed discussion of the waste qualification process is presented in DOE/NE/44139-49, "Cement Waste Form Qualification Report-WVDP PUREX Decontaminated Supernatant."¹ This report briefly summarizes waste form qualification and testing work, and then focuses on full-scale testing, recipe modification, qualification testing, and cement processing operations that took place during supernatant and sludge wash campaigns conducted at the West Valley Demonstration Project (WVDP).

2.0 LIQUID HIGH-LEVEL WASTE CHARACTERIZATION

A waste characterization program was initiated at the WVDP shortly after site operations began in February 1982 and is described in DOE/NE/44139-14, "High-Level Waste Characterization at West Valley, Report of Work Performed 1982-1985."² Results from the extensive characterization done were used to determine the complete chemical and radiological makeup of the alkaline supernatant in Tank 8D-2, refine estimated solids content, and evaluate homogeneity of the wastes. The chemical composition of the supernatant derived from this work is given in Table 2-1. The radiochemical composition of the supernatant is given in Table 2-2.

Characterization results were central to the development of process chemistry and a flowsheet for decontamination and cement recipe formulation. Analysis information was used for sludge mobilization and vitrification planning.

Recipe formulation work began with studies conducted at the Westinghouse Research and Development Center from 1983 to 1984 that used several identified waste streams to develop cement recipes with maximum waste loadings.³ Laboratory testing was done with Type I portland cement and simulated supernatant according to guidance on test methods and acceptable results given in the NRC Branch Technical Position on Waste Form Qualification, May 1983.⁴

Table 2.1 - 8D-2 Supernatant Chemical Composition

Compound	Wt% Wet Basis	Wt% Dry Basis	Total Kg in Supernatant
NaNO ₃	21.10	53.38	602,659
NaNO ₂	10.90	27.57	311,326
Na ₂ SO ₄	2.67	6.76	76,261
NaHCO ₃	1.49	3.77	42,557
KNO ₃	1.27	3.21	36,274
Na ₂ CO ₃	0.884	2.24	25,249
NaOH	0.614	1.55	17,537
K ₂ CrO ₄	0.179	0.45	5113
NaCl	0.164	0.42	4684
Na ₃ PO ₄	0.133	0.34	3799
Na ₂ MoO ₄	0.0242	0.06	691
Na ₃ BO ₃	0.0209	0.05	597
CsNO ₃	0.0187	0.05	534
NaF	0.0176	0.04	503
Sn(NO ₃) ₄	0.00859	0.02	245
Na ₃ U ₂ O ₇	0.00808	0.02	231
Si(NO ₃) ₄	0.00806	0.02	230
NaTeO ₄	0.00620	0.02	177
RbNO ₃	0.00416	0.01	119
Na ₂ TeO ₄	0.00287	0.007	82
AlF ₃	0.00271	0.007	77
Fe(NO ₃) ₃	0.00152	0.004	43
Na ₂ SeO ₄	0.00054	0.001	15
LiNO ₃	0.00048	0.001	14
H ₂ CO ₃	0.00032	0.008	9
Cu(NO ₃) ₂	0.00022	0.005	6
Sr(NO ₃) ₂	0.0013	0.004	4
Mg(NO ₃) ₂	0.00008	0.002	2
TOTAL	39.53	100.00	1,129,038
H ₂ O (by difference)	60.47		1,727,164

Table 2.2 - 8D-2 Supernatant Radiochemical Composition

Species	1 ft* $\mu\text{Ci/gm}$	5 ft	15 ft	% Relative Standard Deviation
Cs-137	2.86 E^0	2.80 E^0	2.84 E^0	0.2
Cs-134	2.36 E^2	2.32 E^2	2.35 E^2	3.0
Sr-90	1.14 E^3	1.13 E^3	1.12 E^3	1.0
Sb-125	5.7 E^5	5.5 E^5	5.4 E^5	12.0
Ru-106	$< 1.5 \text{ E}^5$	$< 1.5 \text{ E}^5$	$< 1.5 \text{ E}^5$	NA
Ce-144	$< 7.6 \text{ E}^7$	$< 7.6 \text{ E}^7$	$< 7.6 \text{ E}^7$	NA
Rare Earth B	2.1 E^4	1.5 E^4	2.7 E^4	3.0
Am-241	$< 1.5 \text{ E}^5$	$< 1.5 \text{ E}^7$	$< 1.5 \text{ E}^7$	NA
Am-243	$< 2 \text{ E}^7$	$< 2 \text{ E}^7$	$< 2 \text{ E}^7$	NA
Cm-244	$< 6 \text{ E}^8$	$< 6 \text{ E}^8$	$< 6 \text{ E}^8$	NA
	$\mu\text{gm/gm}$			
Pu-238	0.0024	0.0031	0.0027	3.0
Pu-239	0.1302	0.1545	0.1461	3.0
Pu-240	0.0251	0.0307	0.0301	3.0
Pu-241	0.0051	0.0066	0.0060	3.0
Pu-242	0.0021	0.0025	0.0024	3.0
U-233	0.017	0.019	0.018	8.0
U-234	0.014	0.017	0.016	8.0
U-235	0.967	1.101	1.044	3.0
U-236	0.097	0.108	0.105	8.0
U-238	55.145	63.182	59.865	0.3

* Samples taken at three levels: 1ft, 5ft, and 15 ft below the surface of the liquids

2.1 Waste Form Requirements

The main purpose of the NRC's 1983 Branch Technical Position on Waste Form Qualification was to provide guidance on testing methods and results that could be used to show compliance with waste form requirements given in 10 CFR Part 61, "Licensing Requirements for Land Disposal of Radioactive Waste." These requirements establish a waste classification system, and relate the classification system to land disposal requirements.⁵

The link between waste form qualification test recommendations and land disposal requirements is given in 10 CFR Part 61.56. It states that a waste form must be structurally stable, and able to maintain physical dimension and form under expected disposal conditions. These include the weight of overburden and equipment, presence of moisture and microbial activity, and internal factors such as radiation effects and chemical changes. Meeting Part 61 criteria should result in a waste form that maintains gross physical properties, and is easily identifiable over a period of 300 years. Accordingly, an appropriate waste form should remain stable if it:

- Is solid and stable after disposal;
- Has no free standing or corrosive liquid;
- Resists degradation caused by radiation effects;
- Resists biodegradation;

- Remains stable under compressive loads in the disposal environment:
- Remains stable if exposed to moisture or water after disposal; and
- Is compatible with the solidification medium used or container in which it is placed.

The testing methods and guidelines to achieve these criteria were given in the 1983 Branch Technical Position. They included recommendations for waste form qualification testing, test specimen preparation, statistical sampling and analysis, waste characterization, process control plan requirements, surveillance requirements for long-term results, and mishap reporting. These guidelines were used to develop and test cement recipes for encapsulating the salt solution that would result from decontaminating the supernatant in Tank 8D-2.

3.0 CEMENT CHARACTERISTICS

3.1 Cement Chemistry

Portland cement is a low alkali, hydraulic cement that forms a hardened paste when water is added to it. It is manufactured using naturally occurring and secondary materials that contain four primary chemical elements: calcium, silicon, aluminum, and iron. Calcium sulfate, as gypsum, is added in the final stages of production to regulate the setting time of the final product.

During manufacturing, the following four compounds are added to the basic cement mixture (i.e., calcium, silicon, aluminum, iron, and gypsum) that determine the characteristics and uses of the five major types of portland cement produced:

- Tricalcium silicate (C_3S)—responsible for initial set and early strength;
- Dicalcium silicate (C_2S)—contributes to increasing strength beyond one week;
- Tricalcium aluminate (C_3A)—liberates heat, and contributes slightly to early strength; and
- Tetracalcium aluminoferrite (C_4AF)—assists in cement manufacture.

3.2 Cement Hydration

When water and cement are mixed, a series of chemical reactions begins that result in stiffening, hardening, evolution of heat, and finally, the development of long-term strength. The overall process is known as cement hydration because water-containing compounds form as the reactions occur. The hydrates that form determine the characteristics of the hardened cement paste. The following hydration reactions illustrate the basic cement hydration process:

Basic Cement Hydration

Tricalcium silicate + water

Tobermorite gel + calcium hydroxide

Dicalcium silicate + water

Tobermorite gel + calcium hydroxide

Tricalcium aluminate + water + calcium hydroxide

Tetracalcium aluminate hydrate

Tetracalcium aluminoferrate + water + calcium hydroxide

Calcium aluminoferrite hydrate

Tricalcium aluminate + water + gypsum

Calcium monosulfoaluminate hydrate

The first chemical compounds to react are the aluminates, tricalcium aluminate (C_3A), and tetracalcium aluminoferrite (C_4AF). They immediately form calcium aluminate hydrates. These hydrates provide structure, and help to stiffen the cement paste. As sulfate from gypsum in the cement mixture enters into solution, it reacts with the aluminates, coating them with a calcium sulfoaluminate hydrate called ettringite. This ettringite keeps water from combining too quickly with the highly reactive aluminates, helping to keep the paste plastic.

Within hours, water reacts with tricalcium silicate (C_3S) to produce calcium hydroxide and cement gel. As time goes on, the calcium sulfoaluminate hydrate (i.e., ettringite) reacts with tricalcium aluminate (C_3A) and water to form a different calcium sulfoaluminate hydrate, and the aluminates begin to hydrate again. The tricalcium aluminate (C_3A) reacts with water and calcium hydroxide to form tetracalcium aluminate hydrate. After several days, very little of the ettringite remains. Dicalcium silicate (C_2S) begins to hydrate within the first several days. Both calcium silicates, C_3S and C_2S , lead to the formation of calcium hydroxide and calcium silicate hydrate (CSH), which is also known as tobermorite or cement gel. This is the principal binder in the system.

Based on the characterization of the chemical composition in Tank 8D-2, Type I portland cement was tested as the binding agent for the salt solution that would result from decontaminating the supernatant in Tank 8D-2. It is the type of portland cement most often used for solidification and stabilization of wastes.

4.0 SUPERNATANT

4.1 Recipe Development

Actual recipe formulation work was done at the Westinghouse Research and Development Center using Type I portland cement and a simulant of the alkaline supernatant formed during reprocessing operations. This supernatant resulted from neutralization of plutonium/uranium extraction (PUREX) process wastes. The chemical composition of the simulant is given in Table 4.1.

Table 4.1 - Chemical Composition of Simulated Supernatant

Salt	Weight Percent Dissolved in Water (Total Solids)
NaNO ₃	21.1
NaNO ₂	10.9
Na ₂ SO ₄	2.67
NaHCO ₃	1.42
KNO ₃	1.27
Na ₂ CO ₃	0.884
NaOH	0.614
K ₂ CrO ₄	0.179
NaCl	0.164
Na ₃ PO ₄	0.133
Na ₂ MoO ₄	0.024
NaF	0.016
Na ₃ BO ₃	0.020
Total Solids	39w/o

Work began with jar testing. This test method was used to select the most promising recipe for full scale encapsulation tests. After the most promising recipe was selected, 6 × 12 inch cylinders were prepared for waste form qualification testing according to the methods and guidelines prescribed in the NRC's 1983 Branch Technical Position.

All waste forms tested had compressive strengths that exceeded the minimum guideline for compressive strength (i.e., 50 psi). They also had a leachability index greater than that given in the NRC Branch Position (i.e., 6). Waste forms with high salt content (i.e., greater than 43% total solids) did not perform well for all requirements. Based on this observation, process limits were set to a nominal 39% weight total solids, with a maximum of 41% weight total solids. The recommended recipe used a water-to-cement ratio of 0.61, with a range of 0.54 to 0.70.

4.2 Full-Scale Testing

Full scale testing of the qualified cement recipe began at the WVDP in early 1988. Using simulated supernatant at 39% weight total solids, tests were run in the Cement Solidification System (CSS) with equal weights of supernatant and cement. These tests produced a product with high air entrainment, low density caused by rapid hydration, and lower than expected compressive strength due to air entrainment.

Air entrainment was attributable to mixing conditions. Foaming observed during recipe development and qualification testing had been eliminated by vibration, which was not possible to do with a full-scale system. Samples of the same supernatant and cement mixture used in the CSS were tested in the Analytical and Process Chemistry Laboratory (A&PC Lab) to try to duplicate the foaming seen in the CSS. A high-speed blender run at its lowest speed could reproduce approximately the same amount of foaming as that seen in the CSS. Careful analysis of the simulated supernatant used in the A&PC Lab showed that it was acceptably close to the simulated supernatant used during recipe development. Recipe verification and the ability to reproduce foaming made it possible to test a range of additives in the A&PC Lab. A silicone-based food grade additive, GE AF-9020 antifoam, was the most promising additive tested. After additional testing to determine the ideal concentration and mix time, full-scale testing resumed.

The first batch of simulated supernatant and cement prepared using the revised recipe did not produce an improved waste form. The amount of antifoam was doubled to correct for possible scale-up effects. Mix times and the order of addition were also modified to improve recipe performance. These modifications and adjustments were successful in producing an improved waste form.

4.3 Verification Testing and Recipe Modification

Verification testing began once full-scale testing of the modified recipe was completed. It was done in the A&PC Lab using an actual sample of supernatant that had been decontaminated in the A&PC Lab hot cell with zeolite IE-96®. Three two-inch cubes were prepared with the proper ratio of supernatant, antifoam, and cement mixed and poured well, with little air entrainment. However, the cubes underwent phase separation after about 30 minutes. Bleed water was evident within one hour. It increased to about 5 percent of the original liquid volume as time went on. Chemical analysis showed that the supernatant was chemically and radiochemically unaltered. Setting did not occur until several days after the pour. The bleed water was not reabsorbed. This suggested the presence of a set retardant in the sample of supernatant used. A records search was initiated to learn how much organic material had been added to Tank 8D-2 during reprocessing operations because organic materials are known set retardants.

Several organic materials had been used during reprocessing operations and plant decontamination activities. Plant records showed that about 30,000 pounds of citrate, oxalate, and tartrate had been used during plant decontamination.⁶ A literature search was done and experts consulted to evaluate the effect of organic acid salts or residues on cementation of the waste. Lab-scale testing was also initiated to modify the existing recipe.

A variety of additives were tested, including bentonite clay, attapulgite clay, calcium chloride, hydrated lime, calcium nitrate, sodium silicate, and mixtures of calcium chloride or nitrate and sodium silicate. These additives were used with both chromated and nonchromated synthetic supernatant with organic acid salts added. A mixture of calcium nitrate and sodium silicate demonstrated the best performance during lab-scale testing. Once this was established, a range of variables was identified for further evaluation including: order of addition; amount of additives used; range of organic acid concentrations needed to produce acceptable results; and increase (if any) in total process volume caused by reduced waste loading.

After these variables were evaluated, a small amount of waste form was produced using the enhanced recipe and actual decontaminated supernatant. This waste form had high density, no bleed water, and compressive strength greater than about 600 psi after eight days of curing. These results clearly showed that the enhanced recipe was ready for full-scale testing.

Full-scale testing resumed in the CSS using the enhanced recipe to make several drums with accurate simulant (i.e., simulant with the correct ratio of chromates and total organic carbon). An excellent correlation between laboratory and full-scale testing was observed. Based on recipe performance under actual operating conditions, a supplementary qualification testing program was initiated to ensure that use of the enhanced recipe would not degrade the performance characteristics of the originally qualified recipe. Results of this testing showed that product performance was improved with respect to compressive strength, thermal cycling resistance, and compressive strength following water immersion. This success was achieved using a recipe that varied less than 2 percent in elemental composition from the originally qualified recipe.

4.4 Short- and Long-Term Waste Form Testing

Test plans were prepared for both short- and long-term testing of the final cement waste form. Each test plan required core samples to be taken from production drums using a defined core-boring technique. This technique was designed to yield core samples that could be cut, measured, and tested according to the method prescribed in ASTM C-39: Standard Test Method for Compressive Strength of Cylindrical Concrete Specimens.⁷

Short-term testing involved taking core samples after a minimum cure period of 40 to 70 days. To demonstrate compliance with NRC Branch Position and Part 61 criteria, these samples were tested for homogeneity, leach resistance, and compressive strength.

Long-term testing involved taking core samples from drums selected from a single production run. Twenty drums processed during July 1988 were selected for this purpose. Samples were then taken and tested periodically for five years. The long-term test plan called for taking two core samples from the upper, middle, and lower sections of a test drum. One core sample from each level was reserved for visual inspection and compressive strength testing according to ASTM C-39. Remaining core samples were bagged and stored in the controlled environment of the on-site Drum Cell (i.e., greater than 50°F). At six month intervals, these core samples were inspected for signs of cracking or spalling. Testing began with six cores taken from one drum after a cure period of 225 days. Samples continued to be taken from nine more drums until a cure period of 1842 days had been reached. Ten remaining drums were not tested, but stored in the Drum Cell for potential testing in the future. A summary of short- and long-term test results is given in Table 4.2.

Compressive strength test results for cores taken from each drum ranged from 620 psi to 1960 psi. The curing curve plotted for this data is shown in Figure 4.1. Average and individual results from all short and long-term tests exceeded the 60 psi minimum value given in the 1983 NRC Branch Position. Three out of ten long-term cores tested showed compressive strength averages that were lower than other cores tested. These results are attributable to expected random scatter, and differences in individual operator techniques used during core boring.

Table 4.2 - Short- and Long-Term Waste Form Test Summary

Criteria	Supernatant Waste Form Results*
Compressive Strength >60 psi	Avg. 890 psi after 74 days of cure Avg. 1260 psi after 1842 days of cure
Compressive Strength Following 90-day Immersion >60 psi	650 psi
Homogeneity	Top: 7.65E 03 $\mu\text{Ci/g}$ 1 std. dev 7. 7.E 04 Middle: 8.15E 03 $\mu\text{Ci/g}$ 1 std. dev. 1.3E 03 Bottom: 7.69E 03 $\mu\text{Ci/g}$ 1 std. dev. 3.2 E 04
Radionuclide Leach Indices >6	Cs-137: >6.5 Tc-99: >6.6 Sr-90: >9.4 Pu: >15.2

* Qualified Recipe Parameters: 37 - 41 weight % solids. pH 10. % total salts (SO_4) 4.0. and water-to-cement ratio 0.61-0.63

Figure 4.1

4.5 Change in NRC Branch Position Guidance

Original NRC waste form qualification guidelines described what was needed to prove that a waste form would remain stable under actual disposal conditions. These guidelines were based on conditions at one licensed disposal facility. Recognizing that waste forms would be taken to a number of different disposal facilities, the NRC modified the guidelines to support disposal under a greater range of conditions. For example, compressive strength requirements were increased to reflect changes in the depth at which waste forms might be disposed.

Guidelines also were updated to address waste form issues that arose during recipe development at various facilities. Field experience and laboratory testing of cement waste forms at several facilities showed that unique chemical and physical interactions can occur between cement constituents and chemicals and compounds found in waste. The revised guidelines were expanded to include an appendix that provides detailed guidance on cement waste form testing, and associated acceptance criteria. Specifically, it updated criteria for compression strength testing, thermal cycling, irradiation, biodegradation, leach testing, immersion testing, free standing liquids, and full-scale testing. It also updated criteria for qualification test specimen preparation (i.e., mixing, curing, and storage), statistical sampling and analysis, waste characterization, process control plan specimen preparation and examination, surveillance of specimens, and mishap reporting. Cement waste form testing and acceptance criteria used at the WVDP were evaluated and updated to comply with these revised requirements.

5.0 SLUDGE WASH

The presence of sulfates in the sludge layer in Tank 8D-2 posed several problems for vitrification operations. Sulfates are nearly insoluble in glass mixtures. They also cause process problems because they induce foaming in operating melters. Removing sulfates from the sludge in Tank 8D-2 was therefore necessary to ensure the success of radioactive glass-making operations.

Plans were developed to disperse sulfate salts in the sludge layer by adding demineralized water and sodium hydroxide to the tank, and mixing the added liquid with the sludge layer. After allowing the mixture to settle, the resulting liquid (i.e., liquid with sulfate salts) would be decontaminated and processed into the qualified cement waste form, leaving the remaining HLW and sludge to be vitrified. Liquid addition and mixing were scheduled to begin after completion of the final supernatant processing campaign and waste form qualification for the sludge wash liquid.

Chemical and radiochemical analysis done before the start of supernatant processing suggested that the chemical composition of the liquid waste streams processed during HLW pretreatment would vary slightly. Table 5-1 compares the main chemical constituents present at the start of supernatant processing with the sludge wash surrogate used for qualification work, and the decontaminated sludge wash liquid present at the start of sludge wash processing.

Table 5.1 - Chemical Composition of Liquid Waste Streams and Sludge Wash Surrogate Solution

Main Constituents	Supernatant (wt. % solids)	Sludge Wash Surrogate (wt. % solids)	Decontaminated Sludge Wash (wt. % solids)
Na	31	31	30.1
NO ₃	41	27	25.0
NO ₂	18	22	24.1
SO ₄	4.6	14	9.6
CO ₃	2.3	2.6	6.0
K	1.42	0.85	1.28 00
Al	0.03	--	0.12
Cl	.25	0.21	0.29
B	0.003	0.0037	9.6E 03
Cr	0.12	0.15	1.19E 01

The least amount of variability was expected to occur with sodium concentration. Nitrate concentration was expected to decrease, while the nitrite concentration was expected to increase slightly. The greatest change would occur with the sulfate concentration, which would account for 92% of the total salts in the liquid. It was expected that the change in sulfate concentration could be compensated for by reduced waste loading. While supernatant was processed around 39 wt. % total dissolved solids (TDS), sludge wash liquid would be processed around 20 wt. % TDS.

5.1 Tank Chemistry

The final supernatant processing campaign began in November 1990. Review of samples drawn for routine evaluation during this period showed that a slow increase in uranium (U) and plutonium (Pu) concentration was occurring. Processing was suspended, and the Integrated Radwaste Treatment System (IRTS) was placed in standby to evaluate this phenomenon. The evaluation process and related events are discussed in detail in DOE/NE/44139-86, "Liquid Waste Treatment System Final Report."⁹

Waste stream neutralization had been a process requirement maintained during original reprocessing operations to inhibit tank corrosion. Research shows that the solubility of Pu in caustic solutions is a function of pH, with the lowest solubility occurring at 12 to 13 pH. Routine addition of sodium hydroxide to the nitric-acid-based waste stream held the tank pH above 11, thus allowing Pu to precipitate as a hydroxide and become part of the sludge layer.

The concentration of sodium hydroxide (NaOH) in Tank 8D-2 was about 5% at the start of supernatant processing. Some sodium hydroxide was added to process solutions being recycled back to Tank 8D-2 to maintain tank integrity. However, these liquids also were being diluted with demineralized water used for flushing, drainage, and other processing purposes. By the start of the last supernatant campaign, return of various dilute waste solutions had lowered the tank pH to about 10, thus increasing Pu solubility in the liquid. Beyond this change, recycling of liquids back to the tank and operation of the removal pump's floating suction head at low levels created conditions similar to those that would be present during the sludge wash process. The liquid waste being removed from Tank 8D-2 was, in effect, no longer supernatant, but a sludge wash solution. While the increase in Pu solubility made it necessary to put the IRTS in standby, change in the liquid waste stream made it possible to begin waste form qualification work for the sludge wash liquid.

5.2 Recipe Testing

Sludge wash recipe testing began with the preparation of a nonradioactive simulant waste solution. This solution was mixed with Type I portland cement, and used to make 28 two-inch cubes according to a statistically designed Plackett-Burman structure. These screening tests were done to evaluate the effects of 13 variables on gel time, bleed water, and cube compressive strength.

Each variable was tested over a broad range. The water-to-cement ratio was the only statistically significant variable identified, affecting both gel time and compressive strength. Gel time also was found to be affected by the amount of phosphate present in the simulant solution. No variables were statistically significant for the presence or amount of bleed water. Screening results showed that the water-to-cement ratio affected compressive strength nearly 20 times more than any other variable. These observations matched the universal recognition that compressive strength is the single best indicator for long-term stability of the waste form, and provided a key parameter for process control.

5.3 Recipe Qualification

Using the nominal waste form recipe, a waste form mixture was prepared with decontaminated sludge wash liquid around 20 wt.% total dissolved solids (TDS) and Type I portland cement. Mixtures also were prepared around 24 wt. % and 27 wt. % TDS to determine if waste loading could be increased. The amount of sulfate in the decontaminated liquid was increased from 9.1% to 11.3% on a dry salt basis to approximate actual operating conditions. This was done by adding sodium sulfate solution to a heel of decontaminated liquid that remained in the Cement Solidification System (CSS) waste dispensing vessel. The heel had been diluted with water before sulfate addition.

Eleven drums were made with the modified liquid using normal processing equipment and the Process Control Plan (PCP). After the required minimum 28-day cure time, cores were taken from these drums for qualification testing. Tests were done for compressive strength, thermal cycling resistance, leachability, and toxicity characteristic leaching procedure (TCLP) metals retention. No evaluations were done for radiation or biodegradation resistance because the proposed waste form would contain only trace amounts of organic or carbonaceous material.

The cores tested showed excellent compressive strengths, thermal cycling resistance, and TCLP metals retention. Based on these results and the long-term stability of the supernatant waste form, the decision was made to proceed with system preparations for sludge wash processing. As system preparations were getting underway, test cores were readied for 90-day immersion testing in synthetic seawater (i.e., the more aggressive immersion liquid identified).

After 30 days, the immersed cores were examined and photographs were taken. Noticeable deterioration has occurred. The decision was made to begin compressive strength testing of selected cores before completion of the 90-day immersion period. This was done to determine the nature and magnitude of the failure. Cores were crushed after 42, 65, and 90 days of immersion. Compressive strength values for the crushed cores showed a significant decrease in compressive strength that continued to decrease with immersion time. Results were all below the 500 psi requirement.

5.4 Failure Mechanisms

The significant decrease in compressive strength values observed during crushed core testing prompted a thorough review of the entire test program. All aspects of waste form production were evaluated, including the composition of the decontaminated sludge wash solution and the cement waste form.

During the transitional phase between supernatant and sludge wash processing, several events took place that had a potential influence on waste form qualification. As previously noted, the pH of the liquid waste solution being processed had gradually lowered over time through dilution. In addition, IRTS recovery operations were taking place as waste form qualification testing was being conducted. These operations included chemical cleaning of the Liquid Waste Treatment System (LWTS) evaporator with a nitric acid wash solution followed by demineralized water flushes. The cleaning process itself is described in detail in DOE/NE/44139-86, "Liquid Waste Treatment System Final Report." ¹⁰ The rinse solution used to clean the evaporator was made with a very low concentration of nitric acid (i.e., less than two molar), and was followed by a series of flushes. Nevertheless, the system hardware was designed so that residual solution could collect in low flow areas, and ultimately contribute to the low pH (10) of the decontaminated liquid used to make the test drums.

Measures had been taken to ensure that the decontaminated liquid used to make the test drums had a sulfate concentration that approximated actual operating conditions (i.e., 25%). However, preparing solution with a consistent sulfate concentration was quite difficult. Problems dissolving sodium sulfate led to many variations in the actual concentration of sulfates in the decontaminated liquid used to make the test drums. These variations may have affected the waste form.

Finally, test conditions for immersion testing had been modified slightly from those used before. Cores were immersed individually in buckets of synthetic seawater. A liquid volume-to-surface area ratio of 30 cm was used to ensure compliance with Land Disposal Restrictions (LDR) and to avoid the possibility of generating mixed waste. These buckets were stored in an area with a nominal ambient temperature of 35°C. Previous tests had been done by placing three cores into a bucket using a liquid volume-to-surface area ratio of 10 cm. These buckets had been stored in the A&PC Lab under controlled temperature conditions. The increased quantity of synthetic seawater and temperature variation also had some affect on core degradation.

While evaluations were being done, small samples of failed test cores were sent to Westinghouse Savannah River Company for x-ray diffraction analysis. Results of this analysis showed the presence of secondary ettringite. As described in Section 3.1, during the initial stages of the cement hydration process, sulfate from gypsum in the cement mixture enters into solution. This sulfate reacts with aluminates to form a hydrate called ettringite, which coats the cement particles. This coating prevents water from combining too quickly with the aluminates, and helps to keep the cement matrix plastic.

As the hydration process continues, rims between coated cement particles begin to intermesh. This meshing, or bonding, forms the basis for the rigid gel that is referred to as the "final set." Once the complete cement matrix (i.e., final set) has formed and is no longer plastic, destructive expansion reactions can take place. One such reaction occurs when the cementitious solid is exposed to sulfate. This exposure causes calcium aluminate hydrate in the matrix to react with sulfate and form secondary ettringite. Formation of this compound can cause severe damage to the cement matrix through crystal formation. The presence of secondary ettringite detected through x-ray diffraction analysis clearly showed that this type of destructive expansion reaction had taken place.

5.5 Extended Testing

Results of the test program review showed that several factors contributed to the immersion test failure. Hydroxide formation that occurs during the cement hydration process was affected by the low pH of the decontaminated sludge wash solution used to prepare the test drums. In addition, the presence of secondary ettringite in the core samples analyzed proved that severe sulfate attack had taken place. Other factors that may have contributed to the failure included variation in the sulfate concentration of the solution used to make the test drums, and changes in test conditions.

Following evaluation of the immersion test failure, a decision was made to begin qualification testing on cores taken from drums made with actual decontaminated sludge wash solution. These drums were produced after the transition phase between supernatant and sludge wash processing. This decision was made to support the observation that solution used to make test drums during the transition phase was not representative of the actual sludge wash liquid. If the immersion failure was related to the characteristics of the sludge wash liquid, then this could be determined by testing cores samples taken from drums produced just after the transition phase.

Two drums that were produced just after the failed test drums were selected for core sampling. The liquid solution used to make these drums had a pH of 12.0, which was similar to the pH used during earlier recipe development. Two drums produced at a later point also were selected for core sampling. The liquid solution used to make these drums had a pH of 12.6. Core samples from the drums made with 12.0 pH solution were taken at 62, 65, and 82 days of cure. Cores taken at 62 days of cure were used for immersion testing. Cores taken at 65 days of cure were noticeably damp during removal, although compressive strength testing done on these cores showed an average compressive strength of 1140 psi. The core samples taken at 82 days of cure were dry, and showed a higher average compressive strength of 1620 psi. The cores that were used for immersion testing failed. This may have been related to the fact that the drums were not yet fully cured. Core samples taken from the drums made with 12.6 pH solution showed an average compressive strength of nearly 1500 psi after 50 days of cure, and exhibited no dampness during coring. Core samples taken from these drums also passed immersion testing. It is important to note that solution produced after the transition phase exhibited consistent pHs in the range of 12.4 to 12.6. A comparative summary of qualification testing done using sludge wash solutions is shown in Table 5.2.

Table 5.2 - Summary of Qualification Testing with Sludge Wash Solutions and Type I Cement

	Surrogate Sludge Wash	Decontaminated Sludge Wash	Decontaminated Sludge Wash
pH	12.0	10.4	12.0 to 12.6
SO ₄ % of Total Salts	14	11	9.5
Wt. % TDS	20	20 to 27	20
Water-to-Cement Ratio	0.64	0.62 to 0.70	0.66
NRC Criteria			
Compressive Strength > 500 psi	PASS 1247 psi avg.	PASS 1496 psi avg.	PASS 1497 psi avg.
Compressive Strength after 90-day Immersion >500 psi 75% of pre-immersion	PASS 1189 psi 95% of pre-immersion	FAIL all < 500 psi	PASS 1230 psi 82% of pre-immersion
Compressive Strength after 30 Thermal Cycles >500 psi	PASS 1229 psi	PASS 1167 psi	Not scheduled
Radionuclide Leach Index >6.0	PASS Cs-137 >7.8 Tc-99 >7.7 Sr-90 >10.9	Not scheduled	PASS Cs-137 >7.1 Sr-90 >9.9 a-Pu >11.1

5.6 Recipe Modification

Of all the failure mechanisms identified during the review process, formation of secondary ettringite exhibited the greatest potential for affecting long term stability of the final waste form. As briefly discussed in Section 3.1, variations in four compounds present in the basic cement mixture (i.e., tricalcium silicate, dicalcium silicate, tricalcium aluminate, and tetracalcium aluminoferrite) determine the characteristics and uses of portland cement.

The compound that affects ettringite formation in a cement matrix is tricalcium aluminate (C₃A). During the early stages of the cement hydration process, this compound reacts with water to form calcium aluminate hydrates. These hydrates then react with sulfate in the cement mixture to form ettringite (i.e., calcium sufoaluminate hydrate), which slows rapid hydration. As the process continues, ettringite reacts with water and calcium hydroxide to form tetracalcium aluminate hydrate. After several days, very little ettringite remains in the cement matrix. By reducing the concentration of tricalcium aluminate (C₃A) in the basic cement mixture, less tetracalcium aluminate hydrate (3CaO•Al₂O₃•Ca(OH)₂•12H₂O) forms, therefore making it unavailable to react with sulfate. Reductions can be achieved by using Type II portland cement, which is manufactured with a maximum concentration of 8% C₃A, or Type V portland cement, which is manufactured with a maximum concentration of 5% C₃A.

Several options existed to limit sulfate attack. One option was to reduce waste loading. However, this would affect established process parameters like the water-to-cement ratio, and processing characteristics like gel time, compressive strength, and immersion resistance. In addition, lowering the waste loading would result in production of twice as many drums of cement-encapsulated waste as had been planned. Another option was to use a different type of portland cement to produce the waste form. Although both Type II and Type V mixtures were appropriate for use, the Type V mixture offered some advantages, including a more gradual set time and the ability to guarantee a supply that met more stringent specifications (i.e., maximum concentration of 3% C₃A). Based on the ability to obtain a guaranteed supply of cement blended according to qualified recipe specifications, the decision was made to qualify and demonstrate the stability of a nominal waste form at about 30%TDS using Type V portland cement and actual decontaminated sludge wash waste liquid.

A waste form mixture was prepared with a sulfate concentration of 11% on a dry salt basis to approximate actual plant operating conditions. This was done by adding a sodium sulfate solution to actual decontaminated sludge wash liquid that remained in the CSS waste dispensing vessel, as had been done in previous qualification testing. Eleven drums were prepared with the additional sulfate. Ten drums were also prepared without the additional sulfate. Core samples were taken after a minimum of 90 days of cure. These cores provided excellent results for all criteria tested (i.e., compressive strength, immersion resistance, thermal cycling, leach indices, and metals retention). The average compressive strength for 30 cores taken from drums made with solution ranging from 26 to 33 wt. % TDS with water-to-cement ratios of 0.49 to 0.55, was 1230 psi. The average compressive strength for ten cores subjected to immersion testing was 1590 psi, 129% of the pre-immersion average compressive strength. A summary of qualification test results for sludge wash solution stabilized with Type V portland cement is shown in Table 5.3.

Table 5.3 - Summary of Qualification Testing with Sludge Wash Solutions and Type V Cement

Decontaminated Sludge Wash	
pH	12.6
SO ₄ % of Total Salts	10 to 11.4
Wt. % TDS	26 to 33
Water-to-Cement Ratio	0.49 to 0.55
NRC Criteria	
Compressive Strength	PASS
> 500 psi	1230 psi avg.
Compressive Strength after 90-day Immersion	PASS
>500 psi	1590 psi
75% of pre-immersion	129% of pre-immersion
Compressive Strength after 30 Thermal Cycles	PASS
>500 psi	2200 psi
Radionuclide Leach Index	PASS
>6.0	Cs-137 >8.1
	Tc-99 >8.3
	Sr-90 >9.6
	a-Pu >9.6

5.7 Long-Term Test Results

Long-term test plans were prepared to evaluate core samples taken from drums made with both Type I and Type V portland cement. Drums made with Type I portland cement were selected from a production run made in May 1993. These drums were produced using Type I cement and decontaminated sludge wash solution with an average waste loading of 20 wt. % TDS. Drums made with Type V portland cement were selected from a production run made in September 1993. These drums were produced using Type V portland cement and decontaminated sludge wash solution with an average waste loading of 33 wt. % TDS. Testing was done to show compressive strength with minimal cracking and spalling over a period of three years.

Twenty drums were selected from each production run and subjected to testing over the course of three years. After an initial cure period of six months, six cores were taken from the first test drum. As with previous long-term testing, two cores were taken from the upper, middle, and lower sections of the test drum. After visual inspection, one core from each section was reserved for compressive strength testing according to the test method prescribed in ASTM C-39: Standard Test Method for Compressive Strength of Cylindrical Concrete Specimens.¹⁰ The remaining cores were bagged and stored in the controlled environment of the on-site Drum Cell (i.e., > 50°F) for examination at six-month intervals to check for signs of cracking or spalling. This cycle of visual inspection and compressive strength testing was repeated for the next five drums at six-month intervals (approximately). The remaining 14 drums from the 20-drum lot were stored in the Drum Cell for potential testing in the future. A summary of average, long-term compressive strength results for drums made with Type I and Type V cement is shown in Table 5.4.

Table 5.4 - Average Long-Term Compressive Strength Results for Sludge Wash Drums

Type	Process Date	Days of Cure Time	Avg. Compressive Strength
Type I	5/13/93	307	2120 psi
		503	1490 psi
		677	1310 psi
		859	1860 psi
		1040	1920 psi
		1235	2070 psi
Type V	9/01/93	198	983 psi
		393	1090 psi
		567	1110 psi
		748	1120 psi
		939	1740 psi
		1126	1240 psi

To meet NRC criteria, average compressive strength after immersion testing needed to be greater than the qualification mean minus two standard deviations. The qualification mean for drums made with Type I cement was 1102 psi. The qualification mean for drums made with Type V cement was 848 psi. Cores were taken from Type I and Type V drums after six and twelve months of cure. Individual cores were immersed in a one-gallon bucket using a nominal liquid volume-to-surface area ratio of 10 cm, and kept in a laboratory ambient temperature environment. Compressive strength results were greater than the qualification mean for all Type I and Type V cores tested.

Additional testing was done on cores taken from Type I and Type V production drums that represented production drums with the lowest process control plan (PCP) presolidification cube compressive strength values. These cores were subjected to both compressive strength and immersion testing. The average compressive strength for the Type I core was 1640 psi after compressive strength testing, and 1980 psi after immersion testing. The average compressive strength for the Type V core tested was 1710 psi after compressive strength testing, and 1140 psi after immersion testing. These additional tests confirmed that compressive strengths and post-immersion strengths exceeded minimum requirements for both Type I and Type V drums.

At the request of the NRC, compressive strength testing also was done on Type V drums made with 20 wt. % TDS decontaminated sludge wash solution. Cores were taken from a Type V drum with this lower waste loading after 651 days of cure. Cores used for immersion tests showed a post-immersion compressive strength of 970 psi, which clearly exceeded the required strength of 848 psi.

As demonstrated by the testing done on core samples taken from drums produced after the transition phase between supernatant and sludge wash processing, acceptable stability criteria could be achieved by using Type I or Type V portland cement and the sludge wash recipe. Sludge wash recipe qualification testing successfully identified a number of factors affecting waste form stability, including pH and sulfate concentration. The final qualified recipe used Type V portland cement as the binding agent to ensure waste form stability.

6.0 THOREX WASH

6.1 Process Changes

The final phase of HLW pretreatment involved the transfer and blending of about 31,000 liters of acidic thorium extraction process (THOREX) waste held in Tank 8D-4 with washed PUREX sludge in Tank 8D-2. This THOREX waste was the result of reprocessing one core of mixed uranium-thorium fuel during original spent fuel reprocessing operations. Extensive evaluation of the THOREX waste led to the decision to combine the THOREX waste with the PUREX sludge. This was done to minimize variations in the HLW slurry that would be vitrified.

Sodium hydroxide and water were added to Tank 8D-2 to elevate the tank pH before the THOREX transfer. This ensured that the acidic THOREX waste would be rapidly neutralized during transfer operations. After transfer, THOREX waste and PUREX sludge were blended together by using the mobilization pumps in Tank 8D-2 to mix the combined wastes. Neutralization and blending precipitated THOREX solids out of solution and intermixed them with the PUREX sludge. The resulting THOREX solution was then ready to be decontaminated and processed into a qualified waste form similar to that used for supernatant and sludge wash liquids.

6.2 Recipe Testing and Qualification

Waste form qualification for THOREX wash liquids began with preparation of a surrogate THOREX wash solution. This solution was made by chemically adjusting small batches of decontaminated sludge wash with sodium-nitrate, sodium-nitrite, sodium-hydroxide, sodium-borate, and aluminum nitrate to the expected THOREX wash composition. Two solutions were prepared for full-scale testing with pH levels of 13.1 and 12.2 to provide an operating margin for potential plant operating conditions. These solutions were prepared in the CSS waste dispensing vessel in the same way that was used for previous qualification tests. The basic chemical composition of these surrogate solutions is shown in Table 6.1.

Table 6.1 - Chemical Composition of Surrogate THOREX Wash Solutions Used for Full-Scale Testing

Constituent (Wt. % Solids)	pH 13.1	pH 12.3
Na	29.25	30.26
NO ₃	34.36	37.79
NO ₂	25.7	26.00
SO ₄	4.17	4.03
K	0.50	0.46
Cl	0.26	-----
Al	0.21	0.26
B ₄	0.05	0.08
Cr	0.05	0.08
PO ₄	<0.09	<0.13

Waste Concentration: 20.64 to 29.09 wt% TDS with water-to-cement ratios from 0.50 to 0.65

Seventeen drums were made with the pH 13.1 solution, and 13 drums were made with the pH 12.2 solution. All 30 test drums were produced using normal production equipment. Cores were taken from these test drums after 70 days of cure. The core samples tested provided excellent results for compressive strength, thermal cycling resistance, leach indices, and post-immersion compressive strength. A summary of qualification test results for the surrogate THOREX sludge wash solution is shown in Table 6.2.

Table 6.2 - Summary of Qualification Testing with Surrogate THOREX Sludge Wash Solution and Type V Cement

Surrogate THOREX Sludge Wash		
	20 Wt. % TDS	29 Wt. % TDS
pH	12.2 & 13.1	12.3
SO ₄ % of Total Salts	4.2	4.0
Water-to-Cement Ratio	0.55 to 0.65	0.53 to 0.58
NRC Criteria		
Compressive Strength	PASS	PASS
> 500 psi	2360 psi avg.	1830 psi avg.
Compressive Strength after	PASS	PASS
90-day Immersion		
>500 psi	2520 psi	1760 psi
75% of pre-immersion	107% of pre-immersion	96% of pre-immersion
Compressive Strength after	PASS	PASS
30 Thermal Cycles		
>500 psi	2460 psi	2430 psi
	104% of pre-test strength	130% of pre-test strength
Radionuclide Leach Index	Not scheduled	PASS
>6.0		Cs-137 >7.4
		Tc-99 >7.3
		Sr-90 >6.5
		a-Pu >7.4

6.3 Results

Test results showed that the waste form made with the surrogate THOREX wash solution, qualified recipe, and Type V portland cement met and exceeded NRC criteria. Based on these results, core samples were scheduled to be taken from qualification drums made with 20 wt. % and 29 wt. % total dissolved solids after 12 months of cure. Key process control variables to be monitored during actual production runs included water-to-cement ratio, salt concentration, sulfate concentration, and pH. Verification samples were scheduled to be taken and analyzed before solidifying a batch of decontaminated THOREX wash solution. After sample analyses confirmed that the sample met process control limits, a cement cube was prepared and tested to confirm that the process batch would meet established minimum compressive strength values. All analytical results were required to be within process control plan specifications before drum production could proceed. Using this approach, it was possible to ensure production of a quality cement product that was in full compliance with NRC stability criteria for low-level waste forms.

7.0 CONCLUSION

Initial waste form qualification and testing work done at the West Valley Demonstration Project (WVDP) led to development of a basic recipe that could be used to produce a cement-encapsulated waste form capable of achieving U.S. Nuclear Regulatory Commission (NRC) criteria for land disposal of low-level waste (LLW). This recipe used Type I portland cement as the binding agent to solidify and stabilize the LLW. Full-scale testing of the initial recipe successfully identified several factors that influenced waste form production, including mixing conditions and the presence of set retardants in the supernatant that would be decontaminated and processed into the qualified cement waste form. Identification of these factors, and subsequent modification to the initial recipe, resulted in an enhanced recipe that showed improved product performance and varied less than 2 percent in elemental composition from the original formulation. Short- and long-term test results for production drums using this recipe easily achieved NRC criteria (i.e., compressive strength, compressive strength after immersion, compressive strength after thermal cycling, and leach testing).

At the conclusion of supernatant processing operations, efforts began to qualify the Type I recipe for use with sludge wash solutions. Preliminary chemical analysis done before the start of supernatant processing showed that the chemical composition of the sludge wash solution would vary only slightly from the supernatant. Several events took place during the actual sludge wash waste form qualification process that underlined the importance of solution chemistry and its impact on the cement hydration process. Although waste loading for the sludge wash recipe was reduced to compensate for an expected increase in sulfate concentration, this was insufficient to prevent sulfate attack on the test drums made during the sludge wash recipe qualification process. In addition, changes in tank pH were determined to have affected the cement hydration process. Variations in recipe performance led to a more thorough investigation of cement manufacture, a better understanding of how minor constituents influence the cement hydration process, and ultimately, the decision to qualify the recipe for use with Type V portland cement.

During recipe testing performed for all liquid LLW processed (i.e., supernatant, sludge wash, and THOREX wash), immersion testing proved to be the most critical step in achieving results that met or exceeded NRC criteria. Throughout the course of testing sludge wash and THOREX wash recipes, the focus was directed toward achieving satisfactory compressive strength after immersion testing. Variation in test conditions, and the select advantages of full-scale and cube testing also became apparent as sludge wash and THOREX wash recipe qualification work progressed. While preparing cube samples proved to be an efficient method for identifying suitable recipe formulations, full-scale testing eliminated scale-up problems and made it possible to take core samples that provided better, more repeatable test data. The ability to prepare surrogate solutions in a full-scale test environment using actual production equipment was essential to the success of the waste qualification process, especially during recipe modification and extended test work.

As part of the long-term test program to demonstrate compliance with NRC Branch Position and 10 CFR Part 61 criteria, core samples from selected production runs were taken and tested periodically over five years. Results showed that both Type I and Type V portland cement mixtures produced an encapsulated waste form that exhibited no apparent degradation, cracking or spalling. This confirmed that portland cement mixtures are effective binding agents that can be used to stabilize low-level radioactive wastes for long-term disposal.

The waste form qualification and processing program developed at the WVDP resulted in the production of 19,877 drums of stabilized LLW. Long-term test results have shown that these drums meet or exceed all of the requirements for land disposal set forth by the NRC in 10 CFR Part 61. This program remains the single such program to have achieved the goal of solidifying and stabilizing liquid low-level waste by encapsulating waste concentrates in a cement matrix.

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ACRONYMS

A & PC	Analytical and Process Chemistry
ASTM	American Society of Testing Material
CFR	United States Code of Federal Regulations
CSS	Cement Solidification System
DOE	United States Department of Energy
HLW	High-level Waste
IRTS	Integrated Radwaste Treatment System
LDR	Land Disposal Restrictions
LLW	Low-level Waste
LWTS	Liquid Waste Treatment System
NaOH	Sodium Hydroxide
NRC	United States Nuclear Regulatory Commission
PCP	Process Control Plan
Pu	Plutonium
PUREX	Plutonium /Uranium Extraction
% RSD	Percent Relative Standard Deviation
TDS	Total Dissolved Solids
TCLP	Toxicity Characteristic Leachate Procedure
THOREX	Thorium Extraction
U	Uranium
WNYNSC	Western New York Nuclear Service Center

WNYNSC Western New York Nuclear Service Center

DOE/NE/44139-84

WEST VALLEY DEMONSTRATION PROJECT

DOE

**Cement Encapsulation of Low-Level Waste Liquids
at the West Valley Demonstration Project**