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November 13, 1987

Mr. Derek Widmayer
Waste Management/Engineering Branch
Division of Waste Management
Office of Nuclear Materials Safety
& Safeguards
U. S. Nuclear Regulatory Commission
Mail Stop 623 SS
Washington, DC 20555

Dear Mr. Widmayer:

Enclosed is a memo to file written in partial fulfillment to the work required under Subtask 2 of Task 3, FIN A-3175. The memo, entitled "Review of DOE/Westinghouse Documents on Solidification of LLW at West Valley" serves as a partial introduction to the LLW solidification program at West Valley and provides an evaluation of the encapsulation in cement of "decontaminated" supernatant from Tank 8D2.

This is the first in a series of memos; each will deal with a specific waste stream, and will evaluate the encapsulation of the waste in terms of the criteria recommended in NRC's Technical Position on Waste Forms and Container Materials.

If you have any questions or comments, please contact me or Dr. Barry Siskind (FTS 666-5374).

Sincerely,

Biays S. Bowerman

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BROOKHAVEN NATIONAL LABORATORY

MEMORANDUM

DATE: November 3, 1987

TO: File

FROM: B. S. Bowerman BSB

SUBJECT: Review of DOE/Westinghouse Documents on Solidification of LLW at West Valley

1. INTRODUCTION

This memo is the first in a series dealing with the West Valley low-level on-site solidification program. A series is being prepared in order to provide NRC with an analysis of the solidification of specific waste streams on a timely basis, i.e., prior to actual solidification. The first major waste stream to be solidified, the decontaminated supernatant from Task 8D2 is the subject of this memo. The second in the series will address the uranyl nitrate waste stream, which surprisingly is not listed in the Waste Data Sheets.

The documents listed in Table 1 have been reviewed as part of the work (Subtask 2) conducted under Task 2, FIN A-3175. These constitute about half of the documents received from NRC for review. This memo summarizes some of the information contained in the documents, and focuses on those waste streams which are being stabilized (solidified) in cement prior to storage or disposal. The primary intent of this review is threefold: 1) to identify those waste streams requiring stabilization, 2) to identify the method of stabilization, and 3) to evaluate the stabilization method according to the guidance of the NRC Technical Position on Waste Form.

The documents reviewed represent the chronology of the program development at West Valley. One of the difficulties encountered in this review is sorting out what the current plans are for low-level waste (LLW) treatment and disposal at West Valley. For instance, five waste streams described in "Low-Level Waste Cement Encapsulation for West Valley - Final Report" (1984, Document 4, Table 1). According to the Waste Stream Data Sheets (1987, Document 6, Table 1) only three of these five waste streams will be encapsulated in cement; the remaining two will be dewatered and placed in high integrity containers (HICs).

In addition to sorting out the chronology of waste stream treatments, the generation of LLW is apparently changing (or will change soon) after the liquid waste treatment system (LWTS) becomes operational. The LWTS is apparently replacing some of the functions of the low level waste treatment facility (LLWTF) in 1987. (Note that tracking the acronyms for the various operations and systems can be confusing as well.) Hence, the characteristics of

Table 1 Documents Reviewed as of October 28, 1987

1. "Safety Analysis Report, Volume IV, Liquid Waste Treatment System."
2. "Safety Analysis Report, Volume IV, Cement Solidification System."
3. "Safety Analysis Report, Volume IV, Rev. 1, Cement Solidification System."
4. "Low Level Waste Cement Encapsulation for West Valley - Final Report," E. E. Smeltzer, et al., July 1984.
5. "Leachability of Cement Encapsulated Supernatant."
6. "Waste Form (Response) and Waste Stream Data Sheets," Rev. 5, May 1987.
7. "Process Control Program for Solidification of 5-V-1 Flush, Revision 0," September 1986.
8. "Cement Solidification System Analysis," E. E. Smeltzer, September 1986.
9. "Low Level Waste Cement Encapsulation for West Valley - Recipe Development," D. C. Grant, et al., December 1983.
10. "Low Level Waste Cement Encapsulation for West Valley - Compressive Strength," E. E. Smeltzer, et al., December 1983.
11. "Low Level Waste Cement Encapsulation for West Valley - Radiation Stability," E. E. Smeltzer, et al., January 1984.
12. "Leachability of Cement Encapsulated West Valley Low Level Waste Streams," D. C. Grant, et al., February 1984.
13. "Low Level Waste Cement Encapsulation for West Valley - Thermal Cycling Stability," E. E. Smeltzer, et al., June 1984.
14. Low Level Waste Cement Encapsulation for West Valley - Immersion Stability," E. E. Smeltzer, et al., June 1984.
15. Low Level Waste Cement Encapsulation for West Valley - Biological Stability," E. E. Smeltzer, et al., June 1984.

the waste streams to be treated may be somewhat different from those considered in the earlier (1984) documents describing recipe development for the cement waste forms.

Two other general comments are relevant before discussing each waste stream specifically. First, the method of LLW disposal is not made clear, i.e., what wastes will be disposed of on-site and what will be sent for off-site disposal. In particular, there are indications that some of the wastes may be stored for an indefinite period before disposal. Document 4 (Table 1) on page 4-9 implies that the waste forms may be placed outside. If this is the case, then some assurance of proper cement curing prior to exposure to freezing conditions may be necessary.

Secondly, the scope of this task is to review cement solidification activities and waste form qualification testing. Since some of the waste streams will apparently be dewatered in HICs (as of 1987), then some review of the dewatering process and HICs to be used may be necessary for a complete review.

2. WASTE STREAM DATA

Most of the data on waste stream characteristics discussed here is taken from Document 6 (Table 1), since these Data Sheets apparently represent the most recent data (1987). In some of the data sheets, information is deleted, in which case reference to earlier documents is made for this review. The LLW waste stream types are summarized in Table 2. The numbers identifying each waste stream correspond to those used in the Data Sheets by Westinghouse.

2.1 "Decontaminated" Tank 8D2 Supernatant

The largest volume of LLW at West Valley will result from the decontamination of the high level waste liquids and sludges contained in Tank 8D2. The liquid supernatant will be passed through zeolite beds to remove most of the Cs-137, the major radionuclide contaminant, from the supernatant. The effluent from the zeolite beds is the "decontaminated" supernatant, which still contains 3.97 µCi/mL of activity, of which 1.17 and 1.10 µCi/mL, respectively, consist of Cs-137 and its decay daughter, Ba-137m, according to the May 1987 Data Sheets.

Table 1-2 of the Data Sheets lists all radionuclides present in the "decontaminated" supernatant and is reproduced here as Table 3. The list of radionuclides was said to assume a decontamination factor (DF) of 1000 for Cs-137 and for all other radionuclides the DF was said to be one. In addition, the supernatant is diluted with two volumes water for each volume of raw supernatant. The isotope list of Table 3 is thus assumed to be the final radionuclide composition for the wastes to be solidified in cement in the cement solidification system (CSS). Table 3 is essentially identical to the supernatant analysis reported by Rykken.[1] Rykken mentions that high-level THOREX waste contained in Tank 8D4 at West Valley is also to be processed with the sludges from Tank 8D2. However, the THOREX wastes will apparently be mixed with the 8D2 wastes after the supernatant has been removed and the 8D2 sludge is washed.

Table 2 Summary of West Valley Low Level Waste Stream Types and Treatments[a]

Waste Stream	Treatment	Tests Conducted	Comments
1. Supernatant from Task 8D2 (after dilution and decontamination)	Evaporation, then encapsulation in cement	TP tests on simulated, concentrated supernatant wastes (1984)	Class C wastes
2A. First sludge wash 2B. Second sludge wash 2C. Third sludge wash	Evaporation, then encapsulation in cement	TP tests on simulated wastes (1984)	Tests applicable if composition same as supernatant
3. Decon solutions 12.	Filtration and ion exchange	None	Treated water will be recycled or discharged
4. Ion-exchange resin regenerating solution	Not generated as of 1987 (will use resins to "capacity," then dispose of them rather than regenerate)		
5. NO_x scrubber effluents	Encapsulation in cement	None	Class A wastes, no tests needed <u>if segregated</u>
6. Melter feed concentrator overheads	Evaporation	None	Bottoms back to CTS (?), condensates not discussed
7A. LWTS ion-exchange resins	Encapsulation in cement	TP tests on simulated wastes	Class B
7B. LWTS zeolites	Encapsulation in cement	None	Class B

Notes: [a]Based on Waste Stream Data Sheets, Rev. 5, May 1987.

Table 2 (Cont.)

Waste Stream	Treatment	Tests Conducted	Comments
8. LLWTF ion-exchange resins	Encapsulation in cement	TP tests on simulated wastes (1984)	Radionuclide content and Class not specified (1987)
9. Filter backwash (sludges)	Encapsulation in cement	TP tests on simulated wastes (1984)	Class B, tests applicable if these are same as stream 17
10. Low TDS liquids	Ion-exchange	None	Water recycled after treatment
11. Drum decon. solution	Not applicable in 1987 because all drums with excess surface contamination will be overpacked		
13. Spent zeolite eluant	Not applicable - zeolites will not be eluted		
14. Fractionator condensate (HNO_3 recovery)	Will not be generated		
15. Liquids processed in LLWTF (Plant drains and laundry)	Filtration and ion-exchange		No cement - solidified wastes generated
16. FRS spent organic ion exchange resins	Dewatering and HIC		Changed from 1984 when cement encapsulation was expected

Table 2 (Cont.)

Waste Stream	Treatment	Tests Conducted	Comments
17. FRS filter backwash (sludges)	Dewatering and HIC	TP tests on simulated wastes	Changed from 1984 when cement encapsulation was expected
18. LLWTF sludge	Cement encapsulation	TP tests on simulated wastes	Class not specified
19. Burial ground trench pump-outs	Filtration and ion-exchange (LWTS)	None	Treatment of this waste stream was not definite
20. LLWTF resin regeneration solution	Not specified	None	Class not specified
21. LLWTF filter backwash	Not specified	None	Class not specified
22. Decontamination water, interim size reduction facility	Filtration and ion-exchange (LWTS)	None	Class not specified
23. Overheads from CFMUT (?) following HLW tank decontamination	Cement encapsulation	None	Class not known; will be generated after vitrification activities end

Data Sheet, Rev. 5
Nature of Stream
May 1987

Table 3

RADIOACTIVE ISOTOPE CONTENT DECONTAMINATED AND DILUTED SUPERNATANT
(Decayed as of July 1, 1986)

Isotope	T1/2	Type of Decay	Diluted Total ----Ci---- Supernatant	Supernatant Activity Ci/mL
Se-79	6.5×10^4 yr	b	33.3	5.66×10^{-3}
Sr-90	28 yr	b	2.66×10^3	0.47
Y-90	64 hr	b	2.66×10^3	0.47
Zr-93	1.53×10^6 yr	b	0.21	3.66×10^{-5}
Nb-93m	13.6 yr	q	0.21	3.66×10^{-5}
Tc-99	2.13×10^5 yr	b	1,440	0.2466
Ru-106	368 d	b	2.52	4.4×10^{-3}
Rh-106	30 s	b	2.52	4.4×10^{-3}
Pd-107	6.5×10^6 yr	b	1.1×10^{-2}	1.9×10^{-6}
Cd-113	9.0×10^{15} yr	b	8.3×10^{-13}	1.43×10^{-16}
Sb-125	2.73 yr	b	65	1.14×10^{-4}
Te-125m	58 d	q	14.94	2.62×10^{-3}
Sn-126	1.05×10^5 yr	q	0.36	6.3×10^{-5}
Sb-126m	19 m	b/q	0.36	6.3×10^{-5}
Sb-126	12.5 d	b	0.50	8.7×10^{-5}
Cs-134	2.06 yr	b	17.46	3.06×10^{-3}
Cs-135	2.3×10^6 yr	b	0.14	2.4×10^{-5}
Cs-137	30.2 yr	b	6.57×10^3	1.173
Ba-137m	2.5 m	q	6.28×10^3	1.102
Ce-144	284 d	b	6.51×10^{-5}	1.14×10^{-8}
Pr-144	17 m	b	6.51×10^{-5}	1.14×10^{-8}
Pm-147	2.62 yr	b	195.3	0.0342
Sm-151	93 yr	b	1.03	1.76×10^{-4}
Eu-152	13.4 yr	b	4.9×10^{-2}	8.33×10^{-6}
Eu-154	8.2 yr	b	13.41	2.35×10^{-3}
Eu-155	4.76 yr	b	2.46	4.31×10^{-4}
H-3	12.3 yr	b	103	1.8×10^{-2}
I-129	1.59×10^7	b	0.19	3.25×10^{-5}
C-14	5,730 yr	b	92.7	1.63×10^{-2}
Ni-63	100 yr	b	823	0.14

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Table 3 (Cont.)

RADIOACTIVE ISOTOPE CONTENT (CONTINUED)

DECONTAMINATED SUPERNATANT

Isotope	Type of Decay	$T_{1/2}$	Supernatant Ci	Activity)Ci/mL
Np-237	a	2.1×10^{6} yr	ƒ0	0
Np-239	b	2.4 d	ƒ0	0
Pu-238	a	87.7 yr	117	2.05×10^{-2}
Pu-239	a	2.4×10^{4} yr	22.5	3.95×10^{-3}
Pu-240	a	6,537 yr	17	2.93×10^{-3}
Pu-241	b	14.7 yr	1,422	0.249
Pu-242	a	3.8×10^{5} yr	2.3×10^{-2}	4.0×10^{-5}
Am-241	a	432 yr	ƒ0	0
Am-242m	a	152 yr	ƒ0	0
Am-243	a	7,380 yr	ƒ0	0
Cm-242	a	162.8 d	ƒ0	0
Cm-243	a	28.5 yr	ƒ0	0
Cm-244	a	18.1 yr	ƒ0	0
Cm-245	a	8.5×10^{3} yr	ƒ0	0
Cm-246	a	2.4×10^{3} yr	ƒ0	0
			TOTAL	3.97)Ci/mL

2.1.1 Classification of Supernatant Waste Forms

The decontaminated and diluted supernatant, according to the LWTS Safety Analysis Report (Document 1, Table 1), will be sent to the LWTS for concentration by evaporation. The evaporator will concentrate the supernatant to ~46 weight percent (wt%) solids or 50 µCi/mL of Cs-137 if the latter is achieved first. According to Table 1-1 of the Waste Data Sheets, the supernatant stream is ~16 wt% solids containing 1.173 µCi/mL of Cs-137. Using a proportional calculation:

$$\frac{1.173\ \mu Ci/mL}{16\ wt\%} = \frac{x\ \mu Ci/mL}{46\ wt\%} ,$$

the 46 wt% concentrated supernatant will contain ~3.37 µCi/mL of Cs-137. The total radioactivity will be ~11.41 µCi/mL.

The final waste form is prepared by mixing cement with the concentrated supernatant. According to Document 4 (Table 1) an adequate waste form is prepared by mixing the concentrated supernatant with cement so that the final water to cement ratio by weight (w/c) is 0.70 for 39 wt% supernatant and 0.66 for 53 wt% supernatant. A linear change in w/c to 0.68 for the 46 wt% supernatant is reasonable since the latter (interestingly enough) is the midpoint for the waste form simulations and testing conducted in the early (1984) phases of the program. Revision 1 of the Safety Analysis Report for the Cement Solidification System (CSS-SAR-1, or Document 3, Table 1) states that 71 gallon (269 L) drums will be filled to make waste forms. Using data from Table 5.3 of Document 4 and interpolating between the 39 wt% and 53 wt% limits, then a 269 L waste form will contain 261.8 kg (192 L) of 46 wt% supernatant mixed with 206 kg of cement.

From these data, a final activity of 0.647 Ci of Cs-137 per drum of waste can be calculated. This value agrees well with the projected concentration of 0.6 Ci per drum given in Table G.8.2-1 of CSS-SAR-1. The total radioactivity will then be 2.190 Ci per drum when all the isotopes in Table 3 are included.

The activity in Curies per 269 L drum for each of the radionuclides listed in Table 3 can thus be calculated by multiplying the specific activity in the right-hand column of Table 3 by a factor of (0.647/1.173=) 0.552. Table 4 lists the calculated specific activities for radionuclides which are relevant to classification under 10 CFR Part 61. The values for transuranic nuclides (TRU) were calculated by converting activity to total curies (multiply by 0.552) and dividing by the total weight per drum (~468 kg). Table 4 also lists the 10 CFR Part 61 limits for each classes (A, B, C). A comparison of the activity per drum for the concentrated supernatant with the appropriate 10 CFR 61 class limits indicates that the solidified waste must be Class C because the TRU concentration exceeds 10 nCi/gm.

Table 4 Radionuclides in Cement-Solidified Supernatant and 10 CFR 61 Limits

Radionuclide	Ci/drum[a]	Class A Limit[b]	Class B Limit[b]	Class C Limit[b]
Long-Lived Radionuclides				
C-14	0.009	0.215	-	2.15
Tc-99	0.136	0.081	-	0.81
I-129	1.77×10^{-5}	0.00215	-	0.0215
TRU[c]	32 nCi/gm	10 nCi/gm		100 nCi/gm
Pu-241[c]	293 nCi/gm	350 nCi/gm	-	3,500 nCi/gm
Cm-242[c]	0	2,000 nCi/gm	-	20,000 nCi/gm
Short-Lived Radionuclides				
H-3	0.010	10.76	-	-
Co-60	NL[d]	188.3		
Ni-63	0.077	0.942	18.83	188.3
Sr-90	0.259	0.011	40.35	1,883
Cs-137	0.647	0.269	11.84	1,237
Others	NA[e]	188.3	-	-

a. For 71-gal (269 L) drum.
b. Units are Ci/269 L drum unless otherwise specified.
c. Assumes drums contain ~468 kg.
d. NL = not listed in.
e. Not Applicable. Other nuclides fix classification.

This classification is based on the calculations above and assumes that the data used in these calculations are accurate. A significant concern is that the radionuclide concentrations in the decontaminated and diluted supernatant are estimates based on the assumption that the DF for Cs-137 is 1,000 and all other nuclides is 1. There do not appear to be direct measurements of the decontaminated supernatant in any of the documents reviewed to date.

Since the "C" classification is a result of the TRU content of the solidified wastes, then these nuclides must be scrutinized carefully. (Note: Presumably the TRU concentrations have been accurately measured. If the measurements are on the low side by a factor of 3, then the waste may really be greater than Class C.) Table 3 indicates that many TRU concentrations are zero. The sum of all the TRU activities, i.e., total curie content, is 1,578.5 Ci (including Pu-241), according to Table 3. Yet Table G.8.2-2 of the SAR for the LWTS (Document 1, Table 1) states that the total activity of all actinides in the decontaminated supernatant is 1,700 Ci. This discrepancy needs to be explained. In addition, the zero activities for the long-lived TRU nuclides in Table 3 need to be explained. If the DF is one, then some activity should be present, possibly at levels similar to those shown in Table 8.2-2 of Rev. 1 of the SAR for the CSS.

2.2 Supernatant Solidification

Documents 4 through 7 and 9 through 15 in Table 1 present tests and results which are intended to demonstrate that the waste forms produced in the CSS meet the minimum stability criteria recommended in the NRC Technical Position (Rev. 0, 1983).

The chemical composition of the Tank 8D2 decontaminated and diluted supernatant is presented in Table 1-1 of the Waste Stream Data Sheets and reproduced here as Table 5. This composition is the same as that used to make simulated wastes in the TP testing program, with the exception of the "trace" constituents. The latter are those whose concentration is less than 0.02 wt% (dry). Simulated wastes were used to develop cement solidification recipes and conduct the TP tests. Recipes for two solids concentration levels in the supernatant were developed: 39 wt% and 53 wt%. TP tests were conducted on both formulations.

All the test results reported were so-called "full-scale" waste forms. These were prepared in large (~75 L) batches using a full-scale high-shear cement mixer. The cement paste containing the waste was collected in 55-gal drums, and then transferred to plastic cylindrical sample molds approximately 6 inches in diameter by 12 inches high. The molds were vibrated to remove air voids and excess paste was scraped off the top so the sample would have a flat upper surface.

Comment: Since the LWTS will provide a waste stream of ~46 wt% solids, these simulated wastes probably provide an adequate bracket of expected waste form properties. However, no process control program was provided, as called for in the TP. One area of concern regarding the production of actual waste forms is assuring that the waste stream feed is homogeneous and its solids content known. Are there mechanisms which provide assurance of the waste feed composition (solids content) and homogeneity? The solids

Data Sheet, Rev. 5
Nature of Stream
May 1987

Table 5

DECONTAMINATED AND DILUTED SUPERNATANT CHEMICAL COMPOSITION

Compound	Wt. Percent Wet Basis	Wt. Percent Dry Basis	Total Kg in Supernatant[a]
$NaNO_3$	8.53	53.40	542,393
$NaNO_2$	4.40	27.59	280,193
Na_2SO_4	1.08	6.76	68,635
$NaHCO_3$	0.06	3.77	38,301
KNO_3	0.51	3.21	32,647
Na_2CO_3	0.36	2.24	22,724
$NaOH$	0.25	1.55	15,783
K_2CrO_4	0.072	0.45	4,602
$NaCl$	0.066	0.42	4,216
Na_3PO_4	0.054	0.34	3,419
Na_2MoO_4	0.0097	0.06	622
Na_3BO_3	0.0084	0.05	537
NaF	0.0071	0.04	453
$Sn(NO_3)_4$	0.0035	0.02	220
$Na_2U_2O_7$	0.0033	0.02	229
$Si(NO_3)_4$	0.0032	0.02	207
$NaTcO_4$	0.0025	0.02	159
$RbNO_3$	0.0017	0.01	107
Na_2TeO_4(b)	0.0012	0.007	73
AlF_3	0.0010	0.007	69
$Fe(NO_3)_3$	0.0006	0.004	39
Na_2SeO_4(b)	0.00022	0.001	14
$LiNO_3$	0.00019	0.001	13
H_2CO_3	0.00013	0.0008	8
$Cu(NO_3)_3$	0.00009	0.0005	5
$Sr(NO_3)_2$	0.00005	0.0004	3
$Mg(NO_3)_2$	0.00003	0.0002	2
$CsNO_3$	0.000008	5×10^{-7}	0.5
TOTAL	15.965	99.99	1,015,654
H_2O (by difference)	84.035		5,343,032

(a) Assumes 6.3586×10^6 kg decontaminated and diluted supernatant
(b) Assumes Cs DF - 10^3

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content is an important parameter since this combined with the total waste added will determine the water to cement ratio (w/c) in the final waste form.

Table 6 lists the compressive strengths following various cure times and as required after several TP tests. These are discussed in more detail below.

"Baseline" Compressive Strength

The baseline compressive strengths listed in Table 6 all exceed the TP minimum criterion of 50 psi. The average value for the 39 wt% supernatant was 453 ($\pm$ 15) psi, and for the 53 wt% supernatant it was 377 ($\pm$ 12) psi. Presumably the real waste, with a maximum of 46 wt% solids, will have a compressive strength somewhere in between these values, provided the w/c is maintained close to the values specified in the recipe development report (Document 9, Table 1).

None of the documents reviewed address the effects of variations in w/c on waste form properties. This may be covered in "Low Level Waste Cement Encapsulation for West Valley - Tolerance Band Testing" by E. E. Smeltzer, et al., which will be reviewed at a later date.

The "baseline" compressive strength data indicate that the more concentrated supernatant with a slightly lower w/c has a lower compressive strength. This may be the result of higher waste solids loading or the slightly reduced w/c or both.

It is interesting to note that the compressive strength changes over the period of a year. For the 39 wt% supernatant, the solidified waste exhibits a maximum at about six months cure time and then decreases. If the decrease in compressive strength were to continue at the same rate (~80 psi every six months), the compressive strength of the waste form would be less than 50 psi after four years.

The chemical constituents in the supernatant have unknown long-term effects on the waste form's integrity. Compared to normal Portland cement and to the wastes forms prepared with other West Valley waste streams, the compressive strengths of the supernatant waste forms are low. Those made with other waste streams and similar cure times all had compressive strengths in excess of 1000 psi. (See Document 4, Table 1.)

Lea points out[2] that sulfates and nitrates in dilute solutions do not have marked effects on cement; however, he states that gypsum (calcium sulfate) is added to Portland cement mixes to increase set time. The compressive strengths of the West Valley supernatant waste forms indicate that high concentrations of nitrates and sulfates reduce the compressive strength.

The above discussion is not intended to "disqualify" the final supernatant waste forms. The waste forms meet the specified criterion of the TP, exceeding 50 psi easily. However, recent developments indicate that a single compressive strength measurement may not be sufficient to assure stability. For instance, Piciulo et al.[3] measured the compressive strengths of

Table 6 Compressive Strengths of Supernatant Waste Forms (psi)[a]

TP Test	Waste Solids Content	
	39 wt%	53 wt%
"Baseline Compressive Strength		
~38 day cure time	453 (15)	377 (12)
195 day cure time	743 (15)	-
~366 day cure time	663 (164)	580 (53)
Irradiation (~60 day cure)	667 (101)	370[b]
Immersion (~125 day cure)	737 (51)	403 (32)
Thermal Cycling (~150 days cure)	560 (56)[c]	425 (21)[d]

a. Except where noted, the data are the average of three samples. Numbers in parentheses are statistical deviation.

b. One sample only.

c. Five samples.

d. Two samples.

various cement-based formulations incorporating ion-exchange resins in a waste form and found that the strength can be very dependent on the curing conditions as well as on the formulation. Normal Portland cement continues to show an increase in strength for as much as several years,[2] before beginning to decline. Since the 39 wt% supernatant had its maximum strength in less than one year, there may be some question about its meeting the 500 year stability requirement of 10 CFR Part 61 for Class C wastes.

Irradiation

The simulated supernatant waste forms were irradiated to 10^8 rads and compression tested afterward. Only one sample of the 53 wt% concentrated supernatant was available. (Two samples were lost in transit from the commercial radiation facility.) The simulated waste forms met the applicable TP criterion in that the compressive strength following irradiation was greater than 50 psi.

Question: The TP states that waste forms should be exposed to higher doses if the maximum accumulated dose is higher than 10^8 rad. Has the maximum accumulated dose been calculated for the supernatant waste forms? If so, what is the calculated dose?

Immersion Testing

Simulated supernatant waste forms were immersed in water for 90 days and compression tested afterward. These also exceeded the minimum TP criterion of 50 psi compressive strength. Document 14 (Table 1) also states that none of the forms tested showed any signs of cracking during immersion.

Thermal Cycling

Simulated waste forms were tested for thermal cycling stability as suggested in the TP. The environmental chamber was cycled between +60°C and -40°C; however, the interior of the samples achieved a maximum temperature of +40°C and a minimum temperature of -20°C. The samples were subjected to 30 temperature cycles.

The 39 wt% supernatant samples showed no signs of cracking and had compressive strengths in excess of the prescribed 50 psi minimum. However, the 53 wt% specimens did exhibit cracks. Three of the five replicates were so severely cracked that they could not be tested for compressive strength. Those that could be tested showed adequate (>50 psi) compressive strength.

Comment: The failure of some of the waste forms in the thermal cycling tests are a significant concern, because there are indications that the wastes will be stored for some time prior to final disposal. If the wastes are stored, will they be exposed to temperature extremes, or will they be kept in a controlled environment? How long will storage last? Since the real waste forms will have a solids composition in between the two concentrations tested, is it likely (or not likely) that the real (and full-scale) wastes will exhibit cracking when exposed to temperature extremes? Will cracking (if any) adversely affect the long-term stability of these Class C wastes?

Biodegradation

Simulated waste forms were tested following the ASTM G-21 and ASTM G-22 protocols, as described in the TP. The only departure from the TP procedure was that the samples were not suitable for compressive strength testing. The samples instead were slices from two-inch cubes of the simulated waste form. Two of the three 53 wt% samples "failed to resist bacterial growth" in the ASTM G-22 test, and two of the three 39 wt% samples "failed to resist fungi growth" in the ASTM G-21 test.

Document 15 (Table 1) states that growths were not visible to the naked eye in photographs of the samples, and that personnel at the commercial testing lab had identified growth in the tests using a microscope.

Comment: What magnification was required to see the observed growth? Biological degradation is not likely to be a significant concern for cement-based waste forms. However, the TP does state that no indication of growth should be visible, and that subsequent compressive strengths should be measured.

Leach Testing

Leach tests of both simulated supernatant and decontaminated supernatant are reported in Documents 12 and 5, respectively. The decontaminated supernatant was solidified in cement using recipes (i.e., w/c ≈0.70) developed with the simulated supernatant. In both cases, i.e., for simulated and for decontaminated supernatant, two waste streams of 39 wt% and 53 wt% solids were used to make samples.

The leach index for Cs-137 was greater than six for all the samples tested, which meets the applicable TP criterion. The leach indices for Sr-90 and for the sum of Pu-238, 239, and 240 were also measured in the decontaminated supernatant tests. These were greater than 7 and greater than 15, respectively.

Comment: The samples for the leach tests were not prepared using the "full-scale" cement mixer because radioactive materials were used. The w/c was 0.70 for all the samples, both 39 wt% and 53 wt% solids. However, in the recipe development and subsequent tests, the w/c was 0.66 for 53 wt% solid waste forms. This difference in formulation may or may not have a significant effect on leach index measurements.

Full-Scale Tests

The one area in which tests were not conducted was the preparation of full-scale waste forms. The TP recommends that test data be obtained from full-scale products to ensure that their properties are the same as those for small-scale samples prepared for lab tests. No full-scale waste forms were reported in any of the documents reviewed. Hence, there are no data regarding full-scale waste form homogeneity or compressive strength.

References

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3. P. L. Piciulo, et al., "The Effect of Cure Conditions on the Stability of Cement Waste Forms After Immersion in Water," WM-3171-4, Brookhaven National Laboratory, 1987.

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