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TOXICITY CHARACTERISTIC LEACHING PROCEDURE TESTING OF DEFENSE WASTE PROCESSING FACILITY PROJECTED GLASS COMPOSITIONS

by

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TOXICITY CHARACTERISTIC LEACHING PROCEDURE (TCLP) TESTING OF DEFENSE WASTE PROCESSING FACILITY (DWPF) PROJECTED GLASS COMPOSITIONS

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ABSTRACT

Vitrification of Savannah River Site (SRS) high level radioactive waste is scheduled to begin in late 1995. The vitrification operation will take place at the SRS Defense Waste Processing Facility (DWPF). The U.S. Department of Energy has instituted specifications which provide technical criteria which must be met by the DWPF to ensure that the waste glass will be suitable for permanent disposal in a federal geologic repository. Included in these criteria is a specification requiring DWPF to determine whether its high level, radioactive waste glass should also be classified as characteristically hazardous waste. A study was performed, using the anticipated range of glass compositions which will be produced over the lifetime of the DWPF, which definitively proved that DWPF waste glass should not be classified as characteristic hazardous waste.

I. INTRODUCTION

More than 130 million liters of high level liquid waste resides in underground carbon steel tanks at the Savannah River Site (SRS) in Aiken, South Carolina. This waste is to be converted into a stable borosicate glass waste form at the Defense Waste Processing Facility (DWPF). The U.S. Department of Energy has instituted specifications which provide technical criteria which must be met by DWPF to ensure that the waste glass will be suitable for permanent disposal in a federal geologic repository. These specifications are the Waste Acceptance Product Specifications for Vitrified High Level Waste Forms (WAPS). [1]

DWPF waste glass must comply with the WAPS. The Hazardous Waste Specification, WAPS 1.5, requires that DWPF determine whether its waste glass is characteristic hazardous waste by performing the Toxicity Characteristic Leaching Procedure (TCLP)[2] for a bounding range of compositions. The TCLP is an Environmental Protection Agency (EPA) approved test for determining whether Resource Conservation and Recovery Act (RCRA) hazardous metals and organics can be extracted from a waste form. In the case of DWPF waste glass, only the RCRA metals are pertinent as organics cannot survive the high temperatures dictated by the vitrification process.

A study was performed on glasses which spanned the range of projected DWPF compositions. The glasses were doped with RCRA metal concentrations corresponding to levels up to three times higher than a prototypical DWPF glass composition. The doped glasses were tested using the TCLP and the Product Consistency Test (PCT)[3] and the compositions were validated by chemical analyses.

All of the glasses submitted for TCLP testing easily passed the test. The glasses also passed the prototypical PCT test. Analytical results proved the glasses to be amorphous, oxidized and compositionally valid. Based upon the results of this study, DWPF waste glass should not be classified as characteristic hazardous waste, and no further testing should be required to prove compliance with WAPS 1.5, unless there is an unforeseen change in DWPF waste glass composition.

II. TASK DESCRIPTION

Eight different glasses were chosen to bound the range of projected DWPF compositions. RCRA hazardous metals were added to these base compositions for purposes of TCLP testing. The eight base glass compositions were the seven glasses described in the Waste Form Compliance Plan (WCP),[4] and the Environmental Assessment (EA) glass.[5] The compositions of these glasses are provided in Table 1. The seven WCP glasses represent the projected compositions for the first four batches of waste that will be processed by DWPF (Batches 1-4), plus a low viscosity (Purex) composition, a high viscosity (HM) com-

MAJOR GLASS COMPONENTS	CONSTITUENT SLUDGE TYPE							EA glass
weight %	Blend	Batch 1	Batch 2	Batch 3	Batch 4	HM	Purex	
Al_2O_3	3.98	4.87	4.46	3.25	3.32	7.08	2.89	3.2
B_2O_3	8.01	7.69	7.70	7.69	8.11	6.94	10.21	10.9
$BaSO_4$	0.27	0.22	0.24	0.26	0.38	0.18	0.29	
CaO	0.97	1.17	1.00	0.93	0.83	1.00	1.02	1.0
$CaSO_4$	0.077	0.12	0.11	0.10	0.003	trace	0.12	
Cr_2O_3	0.12	0.10	0.12	0.13	0.14	0.086	0.14	
CuO	0.44	0.40	0.41	0.40	0.46	0.25	0.42	
Fe_2O_3	6.95	8.39	7.11	7.48	7.59	4.95	8.54	5.9
FeO	3.11	3.72	3.15	3.31	3.36	2.19	3.78	
Fe_3O_4								2.8
Group A[a]	0.14	0.10	0.14	0.10	0.20	0.20	0.078	
Group B[b]	0.36	0.22	0.44	0.25	0.60	0.89	0.084	
K_2O	3.86	3.49	3.50	3.47	3.99	2.14	3.58	
La_2O_3								0.4
Li_2O	4.40	4.42	4.42	4.42	4.32	4.62	3.12	4.2
MgO	1.35	1.36	1.35	1.35	1.38	1.45	1.33	1.6
MnO	2.03	2.06	1.62	1.81	3.08	2.07	1.99	
MnO_2								1.6
Na_2O	8.73	8.62	8.61	8.51	8.88	8.17	12.14	16.3
Na_2SO_4	0.10	0.10	0.12	0.096	0.13	0.14	0.12	
NaCl	0.19	0.31	0.23	0.22	0.09	0.093	0.26	
NiO	0.89	0.75	0.90	1.07	1.09	0.40	1.21	0.6
SiO_2	50.20	49.81	50.17	49.98	49.29	54.39	44.56	46.3
ThO_2	0.19	0.36	0.63	0.77	0.24	0.55	0.011	
TiO_2	0.90	0.66	0.67	0.66	1.02	0.55	0.65	0.7
U_3O_8	2.14	0.53	2.30	3.16	0.79	1.01	2.89	1.2
ZrO_2								0.4
Other solids[c]								2.9

Table 1. Chemical compositions (on a weight % basis) of the ei[illegible]ase glasses used in the TCLP study.

position and a nominal average waste (Blend) composition. The EA glass is the composition described in the 1982 DOE Environmental Assessment of the DWPF waste form.[6] The EA glass composition has been defined as a chemical durability benchmark. The WAPS require that any DWPF glass produced be demonstrably more durable (as measured by the PCT) than the EA glass.

The RCRA metals were doped into the base glasses to simulate the concentrations projected by the DWPF flowsheet. The RCRA metals represented in this study are: barium, cadmium, chromium, lead, selenium, and silver. Arsenic was not considered because it is not a measurable component of SRS high level waste. Mercury was not considered because it will be recovered during DWPF chemical processing and any residual will not survive the vitrification process. The base glasses were doped with the hazardous metals at two different levels. One level

[a] Group A: radionuclides of Tc, Se, Te, Rb, Mo
[b] Group B: radionuclides of Ag, Cd, Cr, Pd, Tl, La, Ce, Pr, Pm, Nd, Sm, Tb, Sn, Sb, Co, Zr, Nb, Eu, Np, Am, Cm.
[c] Other solids: zeolite, undissolved salts and radionuclides.

RCRA Metal Extraction Levels from TCLP Glasses (ppm)								
RCRA Metal	As	Ba	Cd	Cr	Pb	Hg	Se	Ag
EPA Limit (ppm)	**5**	**100**	**1**	**5**	**5**	**0.2**	**1**	**5**
Batch 1-1	<0.02	0.32	<0.02	<0.09	<0.14	<0.001	<0.01	<0.05
Batch 2-1	<0.02	0.32	<0.02	<0.09	<0.09	<0.001	<0.01	<0.05
Batch 3-1	<0.02	<0.20	<0.02	<0.09	<0.14	<0.001	<0.01	<0.05
Batch 4-1	<0.02	0.36	<0.02	<0.09	<0.14	<0.001	<0.01	<0.05
Blend-1	<0.02	0.32	<0.02	<0.09	<0.14	<0.001	<0.01	<0.05
HM-1	<0.02	<0.20	<0.02	<0.09	<0.14	<0.001	<0.01	<0.05
Purex-1	<0.02	0.65	<0.02	<0.09	<0.14	<0.001	<0.01	<0.05
EA-1	<0.02	0.42	<0.02	<0.09	<0.14	<0.001	<0.01	<0.05
Batch 1-3	<0.02	0.31	<0.02	<0.09	<0.14	<0.001	<0.01	<0.05
Batch 2-3	<0.02	0.24	<0.02	<0.09	<0.14	<0.001	<0.01	<0.05
Batch 3-3	<0.02	0.38	<0.02	<0.09	<0.14	<0.001	<0.01	<0.05
Batch 4-3	<0.02	0.74	<0.02	<0.09	<0.14	<0.001	<.01	<0.05
Blend-3	<0.02	0.28	<0.02	<0.09	<0.14	<0.001	<0.01	<0.05
HM-3	<0.02	0.80	<0.02	<0.09	<0.14	<0.001	<0.01	<0.05
Purex-3	<0.02	0.76	<0.02	<0.09	<0.14	<0.001	<0.01	<0.05
EA-3	<0.02	0.56	<0.02	<0.09	0.21	<0.001	<0.01	<0.05

Table 2. RCRA metal extraction levels as measured by TCLP and compared to EPA limits. All values are reported in parts per million (ppm).

was representative of metal concentrations in the waste as reported in the DWPF Material Balance tables.[7] The second level was three times in excess of that concentration. Both levels accounted for volatilization during melting. Volatility factors were determined based upon the results of a previous study.[8]

All of the batch compositions were calculated to yield 500 grams of glass. Chromium and barium are base components of the WCP glasses (see Table 1), however, existing concentrations of metals were not considered when calculating the dopant levels. Chromium, lead and barium are the primary hazardous species in DWPF glass. Silver, selenium and cadmium are at most trace constituents in the DWPF composition. They were added using the same criteria as the other components, and in many cases were below the detection limits of the analytical instrumentation. The raw material sources for the dopant RCRA metals were: sodium dichromate, lead oxide, barium sulfate, silver nitrate, selenium metal and cadmium hydroxide. Glass batches were prepared by adding these dopant materials, in the appropriate amounts, to the base glass frit. The glass batch was then mechanically agitated for five minutes, poured into an alumina crucible, covered, and melted in an electric furnace. The glasses were heated at 7°C per minute to a temperature of 1150°C and allowed to soak for four hours. The melts were cast into a stainless steel pan to prevent crystallization and mechanically crushed and sieved to ≤9.5 mm. The TCLP protocol requires a 200 gram granular sample with a particle size ≤9.5 mm.[2] The sized 200 gram samples underwent TCLP testing at an independent laboratory recognized by the state of South Carolina as qualified to perform the TCLP.

The doped glasses also underwent analyses by the Analytical Section of the Savannah River Technology Center to verify that the RCRA metals were present in the appropriate concentrations. The Product Consistency Test (PCT) was performed on the doped glasses. The glasses were tested in stainless steel vessels. In addition to the requirements of the standard PCT protocol, the PCT leachates were analyzed for the RCRA metals. This enabled some direct comparison of the two leach tests.

III. RESULTS

All of the glasses submitted for TCLP testing "passed," i.e. none of the glasses released RCRA metals

	METAL OXIDES (weight %)					
	Cr_2O_3	PbO	BaO	AgO	SeO_2	CdO
target level	**0.1004**	**0.1122**	**0.1460**	**0.0027**	**0.0008**	**0.0004**
Batch 1-1	0.4014	0.1955	0.3403	0.0184	0.0511	0.0060
Batch 2-1	0.3899	0.1942	0.3517	0.0202	0.0424	0.0056
Batch 3-1	0.4285	0.1568	0.3995	<0.0024	0.0217	0.0032
Batch 4-1	0.3756	0.0571	0.4629	<0.0024	nd[a]	<0.0012
Blend-1	0.4221	0.0525	0.3721	<0.0024	nd	<0.0012
HM-1	0.3577	0.0425	0.3270	<0.0024	0.0010	<0.0012
Purex-1	0.4070	0.0294	0.4080	<0.0024	nd	<0.0012
EA-1	0.2956	0.0766	0.1920	<0.0023	nd	<0.0012

Table 3. Measured RCRA dopant levels (on an oxide basis) that are present in the TCLP glasses doped at the nominal flowsheet concentration.

	METAL OXIDES (weight %)					
	Cr_2O_3	PbO	BaO	AgO	SeO_2	CdO
target level	**0.3012**	**0.3366**	**0.4380**	**0.0080**	**0.0023**	**0.0012**
Batch 1-3	0.4531	0.4063	0.7277	0.0248	0.0349	<0.0014
Batch 2-3	0.4457	0.3833	0.6953	0.176	0.171	<0.0012
Batch 3-3	0.5709	0.3869	0.7995	0.0100	0.0173	0.0017
Batch 4-3	0.4401	0.4271	0.8721	0.0095	0.0141	0.0043
Blend-3	0.4148	0.3600	0.7795	0.0083	0.0144	0.0020
HM-3	0.3159	0.3150	0.6988	<0.0024	nd	<0.0012
Purex-3	0.5222	0.2921	0.8142	<0.0025	nd	<0.0012
EA-3	0.3369	0.2867	0.5668	<0.0023	nd	<0.0012

Table 4. Measured RCRA dopant levels (on an oxide basis) that are present in the TCLP glasses doped at three times the nominal flowsheet concentration.

into the leachate at a level greater than or equal to the EPA limit. In fact, in nearly every case the metal concentrations in the TCLP leachates were below the detection limits of the instrumentation. The primary exception was barium, and it was still 2 orders of magnitude less than the EPA limit. These results are provided in Table 2 on the previous page.

Tables 3 and 4 represent the metal concentrations of the glass samples as measured by Inductively Coupled Plasma Spectroscopy (ICP). These concentrations are reported on an oxide basis. Chromium, lead and barium, the primary RCRA metal species present in DWPF waste glass, are present in these glasses at levels well in excess of the flowsheet concentations, in almost all cases. In most cases silver, selenium and cadmium are also present. However, silver, selenium and cadmium are trace contituents of the glasses making them difficult to detect.

All of the TCLP glasses also underwent the PCT. Table 5 provides a comparison of the TCLP and the PCT metal extraction results for barium, chromium and lead.

[a]nd = not detected by the analytical instrumentation.

RCRA Metal	Ba		Cr		Pb	
Test Method	TCLP	PCT	TCLP	PCT	TCLP	PCT
Batch 1-1	0.32	0.012	<0.09	0.044	<0.14	0.021
Batch 2-1	0.32	0.040	<0.09	0.013	<0.09	<0.02
Batch 3-1	<0.20	0.012	<0.09	0.060	<0.14	<0.02
Batch 4-1	0.36	0.011	<0.09	0.091	<0.14	<0.02
Blend-1	0.32	0.010	<0.09	0.065	<0.14	<0.02
HM-1	<0.20	0.022	<0.09	0.061	<0.14	<0.02
Purex-1	0.65	<0.004	<0.09	0.172	<0.14	<0.2
EA-1	0.42	<0.004	<0.09	0.058	<0.14	<0.2
Batch 1-3	0.31	0.027	<0.09	0.087	<0.14	<0.02
Batch 2-3	0.24	0.021	<0.09	0.084	<0.14	0.026
Batch 3-3	0.38	0.021	<0.09	0.102	<0.14	<0.02
Batch 4-3	0.74	0.016	<0.09	0.146	<0.14	<0.02
Blend-3	0.28	0.015	<0.09	0.053	<0.14	<0.02
HM-3	0.80	0.031	<0.09	0.074	<0.14	<0.02
Purex-3	0.76	<0.004	<0.09	1.052	<0.14	<0.2
EA-3	0.56	<0.004	<0.09	0.344	0.21	<0.2
EPA Limit (ppm)	**100**		**5**		**5**	

Table 5. Comparison of RCRA metal extraction levels as measured by TCLP and PCT for barium, chromium and lead. The EPA extraction limits are also provided for reference. All values are reported in parts per million.

Test Parameter	TCLP	PCT
leachate fluid	0.1 normal acetic acid	ASTM Type I water
leachate pH	4.93±05	~5-7
agitation	30±2 rpm	none
test duration	18±2 hours	7 days
particle size	<9.5 mm	75-150 μm
temperature	23±2°C	90°C
leachant volume	20X sample mass	10X sample mass

Table 6. Comparison of TCLP and PCT test parameters.

Both the TCLP and the PCT are leach tests, yet the test parameters for the two tests differ a great deal. The basic test parameters are compared in Table 6. All of the glasses were well within the EPA limits regardless of which test was performed. However, the PCT barium results were about an order of magnitude lower, and the PCT chromium results were about an order of magnitude higher, than the corresponding TCLP results. The lead results were below the instrument detection limits for both the PCT and the TCLP tests. The PCT was developed specifically for nuclear waste glasses, and is an aggressive test which is used in modelling long-term chemical durability.[8] Due to its smaller partical size, higher temperature, and longer test duration requirements, it is in general a more stringent measure of overall chemical durability than is the TCLP.

All of the TCLP glasses were characterized by various analytical methods. Chemical composition of the glasses was determined by ICP and Atomic Absorption. Two types of glass dissolutions, sodium peroxide and microwave, were performed to prepare the glasses for ICP testing. Each glass was submitted in triplicate and analyzed in triplicate for each dissolution, providing 18 separate analyses of each composition. The glasses also underwent X-ray diffraction (XRD), X-ray fluorescence (XRF), and Fe^{+2}/Fe^{+3} determinations.[9] XRD spectra verified that the glasses were amorphous. XRF qualitatively confirmed the presence of Ag, Se and Cd in the glasses. Redox testing verified that all of the glasses, with the exception of EA-1, were oxidized with $Fe^{+2}/Fe^{+3} < 0.11$. (EA glass typically has a $Fe^{+2}/Fe^{+3} > 0.11$.) It is important, particularly from a processing standpoint, that DWPF glass is oxidized. An Fe^{+2}/Fe^{+3} ratio of 0.11 has been identified as a limit.

IV. CONCLUSIONS

Based upon the results of this study, DWPF waste glass should not be classified as characteristic hazardous waste. Simulated waste glasses bounding the range of anticipated waste compositions to be processed over the lifetime of DWPF were doped at levels up to three times in excess of prototypical DWPF conditions. All of these glasses successfully passed the TCLP test.

Analytical results proved the glasses to be amorphous, oxidized and compositionally valid. The glasses also passed the PCT test. In addition, the RCRA metal concentrations in the PCT leachates (not typically measured as part of standard PCT protocol) were also well within the EPA extraction limits.

V. ACKNOWLEDGEMENTS

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