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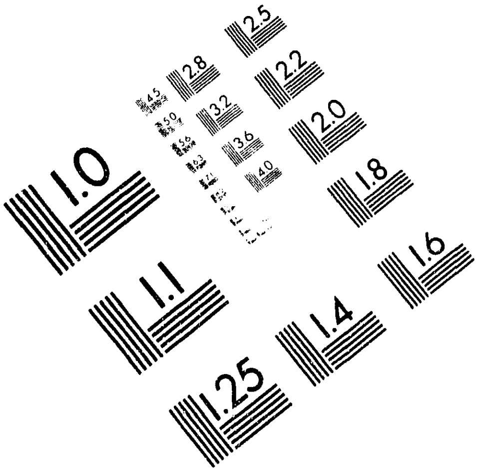

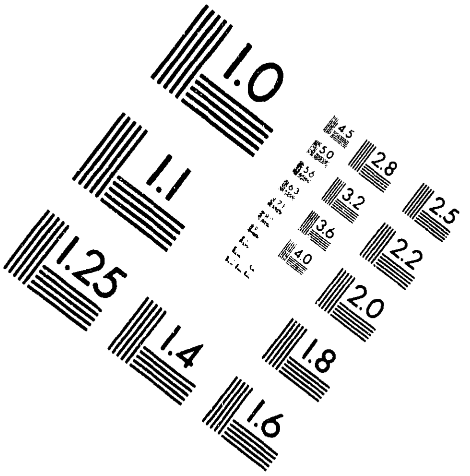

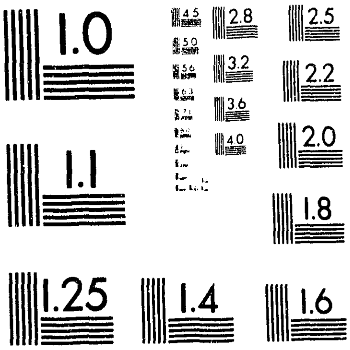

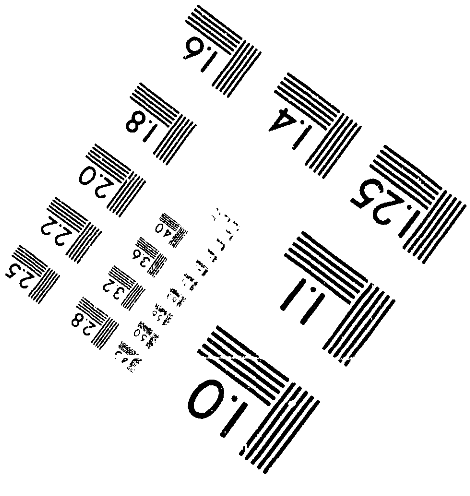

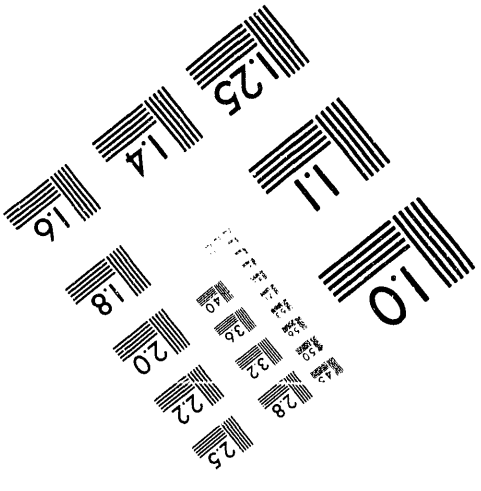

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LABORATORY-SCALE VITRIFICATION AND LEACHING OF HANFORD HIGH-LEVEL WASTE FOR THE PURPOSE OF SIMULANT AND GLASS PROPERTY MODELS VALIDATION

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MASTER

LABORATORY-SCALE VITRIFICATION AND LEACHING OF HANFORD HIGH-LEVEL WASTE FOR THE PURPOSE OF SIMULANT AND GLASS PROPERTY MODELS VALIDATION

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INTRODUCTION

Radioactive wastes generated over the past 50 years at the U.S. Department of Energy's (DOEs) Hanford Site are currently stored in underground carbon steel tanks. Much of the high-level and transuranic (TRU) wastes are stored in double-shell tanks (DST), and are planned for processing into borosilicate glass and grout for final disposal. Undissolved waste solids and recovered cesium, transuranics and rare earths from the DSTs will be processed into glass; and the waste supernate will be processed into grout per the DST Record of Decision (ROD) and Environmental Impact Statement (EIS).

The Hanford Waste Vitrification Plant (HWVP) is being built to process the high-level and TRU waste into canistered glass logs for disposal in a national repository. Testing programs have been established within the HWVP Project to verify process technology using simulated waste. A parallel testing program with actual radioactive waste is being performed to confirm the validity of using simulants and glass property models for waste form qualification and process testing.

The first feed type to be processed by HWVP, and the first to be tested on a laboratory-scale is pretreated neutralized current acid waste (NCAW). The NCAW is a neutralized high-level waste stream generated from the reprocessing of irradiated nuclear fuel in the Plutonium and Uranium Extraction (PUREX) Plant at Hanford. As part of the fuel reprocessing, the high-level waste generated in PUREX was denitrated with sugar to form current acid waste (CAW). Sodium hydroxide and sodium nitrite were added to the CAW to minimize corrosion in the tanks, thus yielding neutralized CAW. The NCAW contains small amounts of plutonium, fission products from the irradiated fuel, stainless steel corrosion products, and iron and sulfate from the ferrous sulfamate reductant used in the PUREX process.

The total inventory of NCAW is contained in two one-million gallon DSTs. Three core samples taken from the two tanks have been characterized and pretreated and are being vitrified and leach tested. Properties of the radioactive waste measured during laboratory process and product testing are being compared to simulant properties and model predictions to confirm the validity of simulant and glass property models work. This paper will discuss the results and status of the laboratory-scale radioactive testing.

EXPERIMENTAL APPROACH

NCAW samples were obtained from the Tank Characterization Program and were pretreated to provide slurry samples for the HWVP vitrification process. Pretreatment included addition of ferric nitrate as a flocculent to promote settling, an initial decant of supernate, and two subsequent wash/settle/decants using 3 volumes of deionized water to 1 volume waste. Results of the core sample characterization and pretreatment are not presented in this paper but can be found in a paper by Tingey, et al., 1991.

Simulant Preparation

Waste simulants were utilized in the laboratory-scale radioactive testing to develop and test procedures and to provide a direct comparison of results with the core samples. These simulants were prepared using a method developed to simulate the history of the waste processing. Major components including Al, Fe, Mn, Ni and Zr were precipitated with NaOH from nitrate solutions and washed to remove the sodium and nitrate. The insoluble minor components (i.e., Ag, Cd, Ce, Cr, La, Li, Mg, Nd, Pb, Pd, Rh, Ru, Si, Te, Ti and Zn) were co-precipitated, washed and blended with the major components. Soluble and slightly soluble minor components (i.e., B, Ba, Ca, Cs, Cu, Na, and Sr) were added directly as oxides, hydroxides, fluorides or sulfates. Sodium was added in multiple forms in order to match the carbonate and anion (i.e., F, Cl, NO_2, NO_3, PO_4, OH and SO_4) concentrations. The simulants were tested on the same apparatus and in the

TABLE I. Differences in Process Steps and Parameters

Process Step/Parameter	101-AZ-C1 (1st Core) 101-AZ-C2 (2nd Core) Simulant 3	102-AZ-C1 (3rd Core) 102-AZ-C1 (Simulant)
Cesium Recycle	Not Added	Added
Washed Solids Concentration	@ 80°C Condensate to Cell	@ 101°C[1], Condensate Collected and Analyzed
Sample sizes @ 125g TO/L	0.164 L (101-AZ-C1) 0.304 L (101-AZ-C2)	0.115 L (102-AZ-C1) in 0.058 L batches
Formic Acid (90wt%) Addition Rate	19.5 to 36.1 gal/min (plant scale equivalent)	2.0 gal/min (plant scale equilavent)
Formic Acid Addition (moles)	3 * (moles NO_3 + 2 * (moles NO_2)	5.5 * moles NO_3 (core) 7.5 * moles NO_3 (sim)
Formating Temp.	95°C ± 3°C	95° ± 1°C
Digestion Temp.	95°C ± 3°C	101°C ± 1°C
Digestion Period	2 hours	4 hours
Recycle Digestion	0 hours, Not Added	2 hours
Offgas Analysis	None	Formating, Digestion, Recycle Addition
Formated Slurry Concentration	125 g total oxide/L (125 g waste oxide/L)	157 g total oxide/L (140 g waste oxide/L)
Target Waste Loading	25%	28%

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[1] Core sample was inadvertently dried out during concentration.

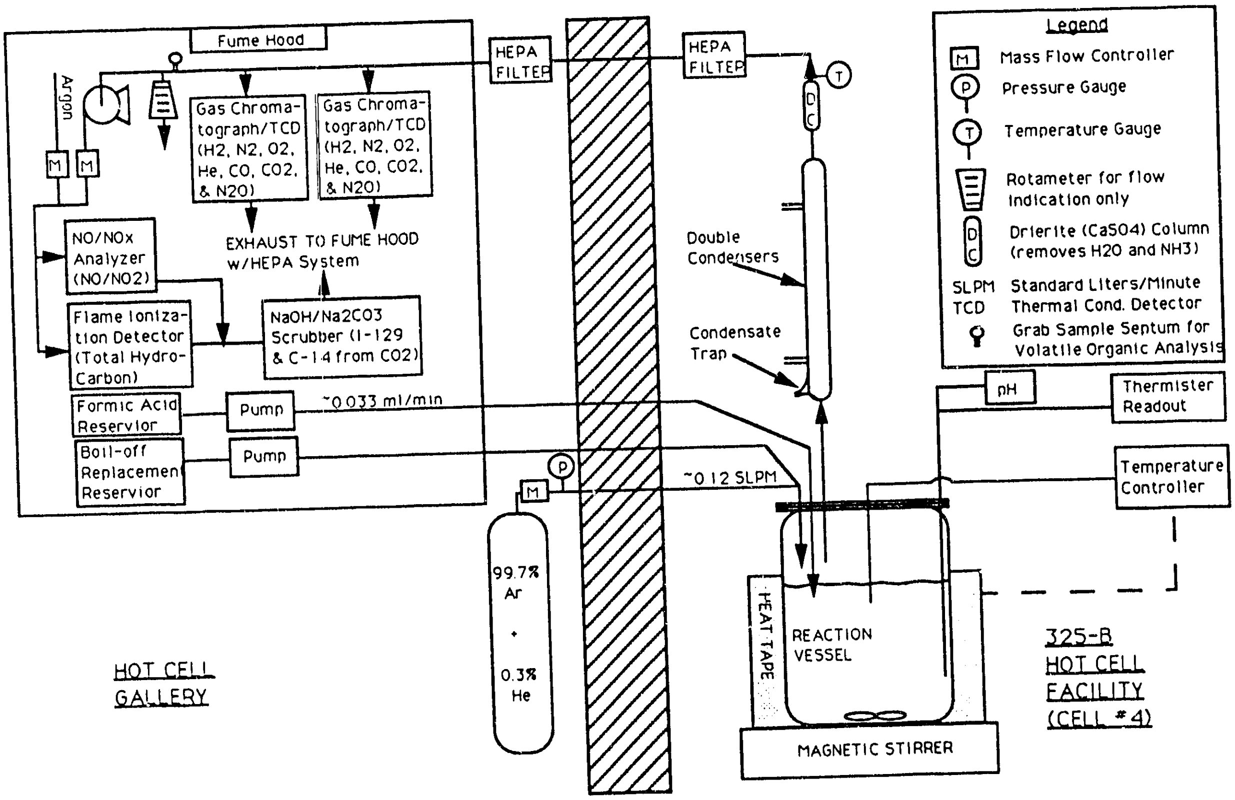

FIGURE II. Radioactive Offgas Measurement System removed in the pretreatment washing steps (Tingey et al., 1991). Comparison of the sodium washed solids concentrations to the HWVP nominal value, indicates that acceptable washing efficiencies are being achieved on a laboratory-scale. Comparison of simulant 102-AZ-C1 to the corresponding core sample shows that compositionally accurate simulants can be prepared using the method described earlier. The simulant composition is based on minimal analysis of one sample, and is likely a much closer match than indicated.

Radionuclide compositions of the washed solids slurries from the three core samples are shown in Table III. Major contributors to the curie content of the glass include ^{90}Sr, ^{137}Cs, ^{144}Ce, and ^{106}Ru. Measured radionuclide concentrations of the core samples were within HWVP specifications for all radionuclides with the exception of ^{129}I, ^{90}Sr, and ^{60}Co. Further analyses are needed to confirm these results. Confirmed concentrations of ^{129}I, ^{90}Sr, and ^{60}Co above maximum limits would result in a change to feed specification and not to the plant flowsheet or design.

Physical and rheological properties were measured on the washed solids, formated slurry and slurry/frit mixture from each of the core samples for comparison to simulant data and correlations. Selected physical property measurements from the core samples and HWVP reference properties are given in Table IV. When the slurry concentrations fell within the design range, the physical and rheological properties were also generally within the design range. A notable exception is the high pH of the slurry/frit mixture for simulant #3 and 101-AZ Core #2, which is characteristic of feed with noble metals and/or slightly soluble frit.

Properties of the radioactive samples are compared to those of simulants and simulant correlations to confirm the validity of using simulants to support design. A few examples of these comparisons are shown in Figures III and IV. Figure III shows good agreement between radioactive and simulant properties for specific gravity versus wt% solids. Figure IV shows that simulant rheologies are consistent with the radioactive samples. Simulant #3 is comparatively more viscous than other simulants for the same wt% solids, which may be related to the high pH.

Offgas data for the radioactive testing and related simulant testing are provided in Tables V and VI and Figure V. The first tests performed were to show comparisons between the radioactive laboratory-scale setup and the bench-scale simulant setup (scale-up factor of 18). Test S1.2 and 3.1 are directly comparable tests on the different setups. The peak gas generation rates and total gas components released compare very well between scales (results within ±10% of averaged values). This is consistent with results of Savannah River Technical Center, which reported agreement between scales (scale-up factor $>10^4$), between hot cell and laboratory tests, and between radioactive and simulant waste (Ha, et al., 1992). These results indicate that laboratory-scale resluts can be accurately scaled up to plant scale to support safety, design, etc.

Tests S2.3 and S2.4 are directly comparable tests between the laboratory setup and the hot cell setup. The hot cell test seemed slightly low, but generally comparable. Peak and total component values were within ±15% of averaged values with the exception of hydrogen, which was about ± 25%. This indicates that results generated in the hot cell are generally comparable with those generated in the laboratory. Tests S2.4 and R1.1 are directly comparable tests between 102-AZ Core #1 and its simulant. Time phased gas generation rates for both tests are given in Figure V. The simulant does not appear to be a good match of the radioactive sample. The differences appear to be compositional differences (CO_3^{2-} and possibly noble metals (i.e., Rh)) caused by inaccurate analysis of the core sample, rather than fundamental differences between simulants and actual waste. The reasons for this conclusion are discussed below.

A few simplified reaction mechanisms hypothesized to account for a majority of the measured offgases are as follows (Wiemers, 1992)(a):

(a) Wiemers, K.D., Langowski, M.H., Powell, M.R., Larson, D.E., 1992. Draft Report "Evaluation of HWVP Feed Preparation Chemistry for an NCAW Feed Simulant--Fiscal Year 1991: Evaluation of Offgas Generation, Reductant Requirements, and Thermal Stability of an HWVP NCAW Feed Simulant." PHTD-C91-03.02C

TABLE III. Radiochemical Composition of Washed Solids Slurries Compared to HWVP Reference

	(Ci/gal @ 0.26 lb oxide/gal)				
				HWVP Reference Feed(a)	
Radioisotope	101-AZ-C1	101-AZ-C2	102-AZ-C1	Nominal	Maximum
H-3	<8.00E-07	<4.99E-07	7.25E-07	2.09E-05	3.63E-05
C-14	8.36E-07	2.45E-07	2.24E-07	2.04E-06	2.54E-06
Co-60	2.13E-02	1.01E-02	4.91E-03	4.24E-04	1.21E-03
Se-79	<7.12E-06	<2.86E-07	<4.48E-06	8.90E-07	1.10E-06
Sr-90	1.09E+01	1.44E+01	5.90E+00	8.42E+00	1.18E+01
Tc-99	1.17E-04	<3.37E-03	1.33E-04	2.12E-03	2.64E-03
Ru-106	6.23E-01	1.01E+00	1.05E+00	1.18E-02	1.41E+00
Sb-125	9.43E-02	1.23E-01	6.59E-02	7.16E-02	4.97E-01
I-129	3.20E-07	7.55E-06	<3.20E-08	3.64E-09	4.60E-09
Cs-134(b)	6.94E-03	NMD	NMD	2.63E-02	3.40E-01
Cs-137(b)	4.27E-01	1.69E-01	1.56E-01	1.02E+01	1.44E+01
Ce-144	9.43E-01	2.06E+00	5.85E+00	2.26E-02	8.43E+00
Eu-154	2.85E-02	7.16E-02	2.66E-02	4.09E-02	9.48E-02
Np-237	1.19E-05	2.53E-05	5.50E-06	4.41E-05	5.63E-05
Am-241	2.13E-02	4.92E-02	2.67E-02	8.02E-02	1.63E-01

(a) Reference values from WHC-SD-HWV-DP-001, HWVP Technical Data Package, Section 13, Rev. 6.

(b) Core samples do not include cesium recycle from supernate.

NMD = Not Measured Directly

TABLE IV. Comparison of Non & Radioactive Physical Properties Data to HWVP Established Limits

Physical Property	Simulant #3	101-AZ Core #1	101-AZ Core #2	102-AZ Core #1	HWVP(a) Nominal	HWVP(a) Design Range
WASHED SOLIDS						
Total solids, wt%	ND	9.4	13.2		4.2	1.8-13
Total Oxides, g/l	69	69	129		31	18-100
Slurry Density, g/ml	1.05	1.04	1.13		1.03	1.02-1.10
Settled solids, vol%	ND	59	66.2		12	7-25
pH	12.6	12.6	12.7		12	11-13
FORMATED SLURRY						
Total solids, wt%	19	15.9	12.2	20.6	15	12-19
Total Oxides, g/l	160	119	101	180	125	100-150
Slurry Density, g/ml	1.11	1.1	1.1	1.16	1.1	1.03-1.15
pH	6.9	5.2		5.0	6	3.5-8
Mean Particle Size, um^2	1.3	1.27	1.42			
SLURRY/FRIT MIXTURE						
Total solids, wt%	37	47	43		40	30-49
Total Oxides, g/l	438	609	479		500	400-600
Slurry Density, g/ml	1.28	1.49	1.2		1.33	1.27-1.45
pH	8.6	5.8	9.4		6	3.5-8
Mean Particle Size, um^2		1.22	1.41			

(a) Reference values obtained from WHC-SD-HWV-DP-001, HWVP Technical Data Package, Section 13, Rev. 6.

(b) Mean particle diameter based on probability number density on length.

NOTES: Values that exceed the HWVP design range are shaded.
ND - Not Determined.

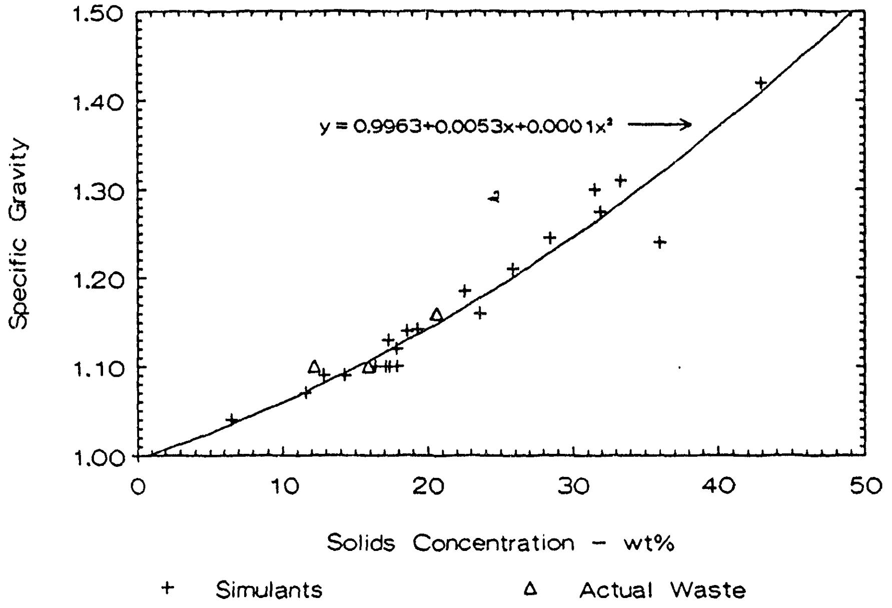

FIGURE III. Specific Gravity of Formated NCAW

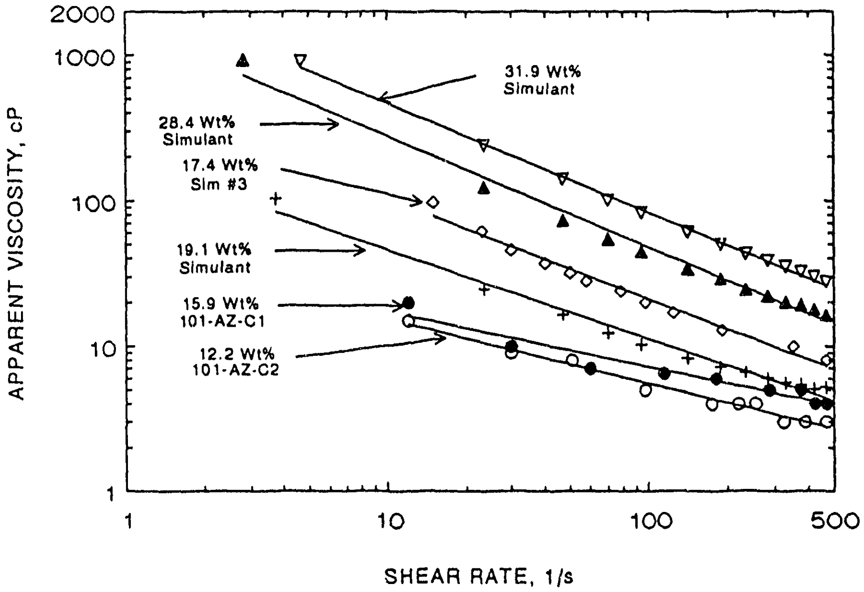

FIGURE IV. Apparent Viscosity of Formated NCAW

TABLE V. Peak Gas Generation Rates (mmol/min/kg oxide)

Test	Description	H_2	CO_2	N_2O	NO
S1.2	Simulant-FY91 HWVP (lab-scale)	2.58	35.0	12.1	1.57
3.1	Simulant-FY91 HWVP (bench-scale)[a]	2.24	42.7	10.9	1.44
S2.3	Simulant - 102-AZ-C1 (out-of-cell)	3.33	44.6	9.18	3.30
S2.4	Simulant - 102-AZ-C1 (in-cell)	1.90	35.7	8.39	2.98
R1.1	102-AZ-C1 (in-cell)	0.43	29.9	3.52	9.83

(a) Results for bench-scale testing were taken from Wiemers et al. 1992. Composition of simulant - FY91 is included in this reference.

TABLE VI. Amount of Gas Components Released (moles/kg oxide)

Test	Species	CO_3 Destruction Phase	Formating Includes CO_3 Phase	Digestion	Recycle	Total
S1.2	H_2	0.0	0.0184	0.131	--	0.149
	CO_2	2.11	2.60	0.94	--	3.54
	N_2O	0.385	0.395	0.011	--	0.406
	NO	0.051	0.052	0.004	--	0.056
3.1	H_2	--	0.057	0.105	--	0.162
	CO_2	--	2.61	0.54	--	3.15
	N_2O	--	0.41	0.004	--	0.414
	NO	--	0.052	0.0003	--	0.052
S2.3	H_2	0.006	0.0582	0.355	0.099	0.512
	CO_2	1.86	3.88	1.30	0.441	5.62
	N_2O	0.165	0.686	0.018	0.0040	0.708
	NO	0.051	0.197	0.021	0.0037	0.222
S2.4	H_2	0.006	0.0346	0.232	0.040	0.307
	CO_2	1.76	3.13	1.00	0.178	4.31
	N_2O	0.164	0.631	0.0094	0.0055	0.646
	NO	0.033	0.152	0.0063	0.0068	0.165
R1.1	H_2	0.002	0.0051	0.0687	0.038	0.112
	CO_2	0.60	1.23	0.479	0.194	1.90
	N_2O	0.007	0.242	0.0022	0.0051	0.249
	NO	0.043	0.628	0.0109	0.0101	0.649

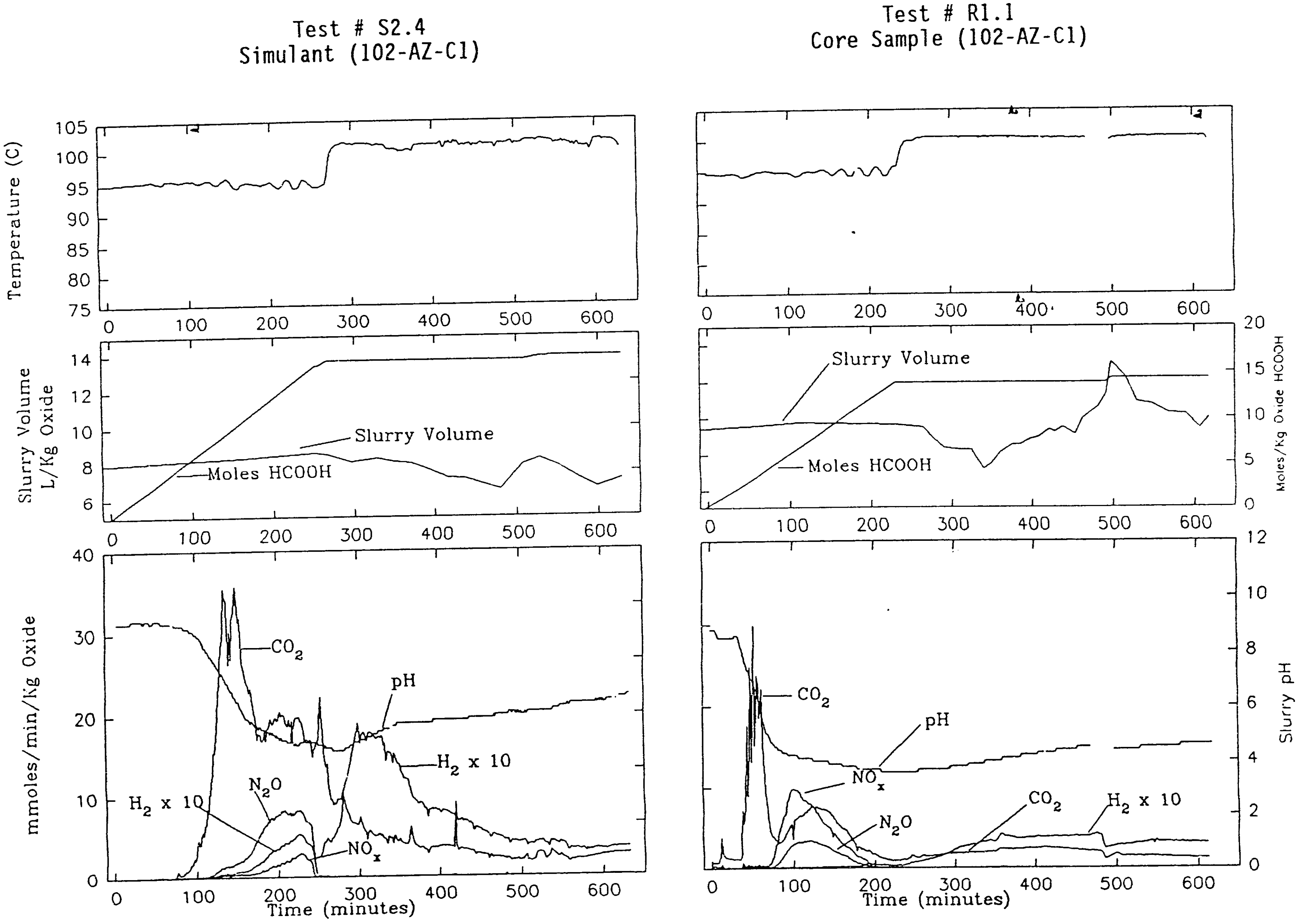

FIGURE V. Comparison of Offgas Profiles for Simulated and Radioactive NCAW Waste

$CO_3^{2-} + 2H^+ \text{-->} CO_2 + H_2O$ eqn 1
$2NaNO_2 + 4HCOOH \text{-->} N_2O + 2CO_2 + 2NaCOOH + 3H_2O$ eqn 2
$3HNO_2 \text{-->} H^+ + NO_{3-} + 2NO + H_2O$ eqn 3
$HCOOH \text{-->} H_2 + CO_2$ (Rh catalyzed) eqn 4
$NaNO_3 + 5HCOOH \text{-->} NH_3 + 4CO_2 + NaCOOH + 3H_2O$ eqn 5
$2NaNO_3 + 5HCOOH \text{-->} 2NO + 3CO_2 + 2NaCOOH + 4H_2O$ eqn 6

The carbonate destruction reaction (eqn 1) is the first phase of the reactions and is represented by the first large CO_2 peak (clearly seen on test R1.1, Figure V). Integration of the peaks during this phase are shown in the third column of Table VI, and compare stoichiometrically (to within 5 - 30% using equations 1 and 2) to known amounts of CO_3^{2-} in the simulants. The amount of CO_2 released from the core sample (test R1.1) during this phase indicates that the amount of CO_3^{2-} in the core sample was approximately 1/3 what was measured and what was added to the simulant. The reduced amount of CO_3^{2-} should result in a steeper pH curve and a reduced N_2O/NO_x ratio, which was observed in the core sample. This difference in carbonate concentration would account for much of the observed differences including steeper pH curve, increased NO_x, reduced CO_2 during the carbonate descrution phase and the remainder of the formating period.

In addition, the core sample test (R1.1) shows several characteristics of a non-noble metal feed whereas test S2.4 shows all the characteristics of a noble metal feed. Characteristics of a noble metal feed include the following (Wiemers, 1992): the N_2O and NO_x releases start around a pH of 7.5 compared to 4.0 - 5.0 pH for non-noble metals feed; a distinct hydrogen peak is observed shortly following decline of the N_2O/NO_x peaks; N_2O/NO_x peaks decrease suddenly compared to a gradual decline for non-noble metals feed; and levels of CO_2 and H_2 that slowly decline throughout digestion and recycle. Test R1.1 exhibits all the characteristics of a non-noble metal feed except for two: 1) considerable H_2 and CO_2 concentrations exist during digestion and recycle (similar to plateau levels measured in test S2.4) and 2) the N_2O/NO_x ratio is higher than expected for nominal non-noble metal feeds, 0.34 versus ≈0.07. These observations indicate a possible reduced noble metals (i.e., Rh) concentration in the core sample or possibly a condition in the core sample that yielded the noble metals inactive during the first half of the test. A verification of noble metals concentration of the core sample is in process. Improved microwave preparation capabilities are being installed in the hot cell to allow better noble metals analysis on radioactive samples using ICP/MS.

The first two core samples and corresponding simulants have been vitrified and leach tested. Results have been compared to predicted results from an empirical model relating glass composition to glass properties (Hrma, et al., 1992). Measured chemical and radiochemical compositions of the glasses are shown in Table VII. These compositions were used as input to the model and used for calculation of normalized releases.

Normalized MCC-1 releases for core sample and simulant glasses are given in Table VIII. The normalized releases for 101-AZ-C1 and 101-AZ-C2 were significantly less than the HWVP reference (28 g/m^2) and the EA glass MCC-1 durability (≈90 g B/m^2). Comparison of laboratory tested simulants to model predictions shows fairly good agreement (within 1 - 3 g/m^2 for B). Comparison of laboratory tests to tests in the hot cell indicates a definite downward bias (nearly 50% reduction in releases) in the hot cell tests. Also observed but not reported here was an increased variance in duplicate samples in the hot cell test. After review of the data and analytical records, two factors (type of leach container and temperature variation within the oven) were suspected as causes for the discrepancies. As indicated prior, fused-silica lined leach containers were used in the hot cell, whereas Teflon containers were used in the laboratory. Analysis of the blank solutions showed significant quantities of silicon in the hot cell tests (6.5 $\mu g/ml$), which was approximately 1/3 the silicon concentrations in the core sample leachates.

A limited scope activity was performed to investigate the differences between leach containers currently being used at HWVP and DWPF (fused-silica, Teflon, and stainless steel). Results of this investigation are provided in Table IX. The MCC-1 leach results in the laboratory show a measurable difference (an average 23% reduction in release, except Si) between Teflon and fused-silica. This difference may be due to the CO_2 and O_2 equilibration in the teflon containers or by increased Si in the fused silica conatiners. The actual cause in not spectulated, but a difference is noted. Note that the silicon release in the fused-silica test was

TABLE VII. Chemical and Radiochemical Composition of Glasses

	wt% Oxide					
	101-AZ-C1	Simulant (101-AZ-C1)	101-AZ-C2	Simulant (101-AZ-C2)	Simulant 3	ATM-10
AL_2O_3	5.22	5.23	2.85	2.86	3.00	6.65
B_2O_3	9.68	9.69	7.38	7.40	10.54	9.17
CaO	0.97	0.97	0.35	0.35	0.91	0.60
Fe_2O_3	10.18	10.19	12.25	12.29	8.81	11.53
Li_2O	3.56	3.56	5.94	5.96	3.75	2.88
MgO	0.77	0.77	0.12	0.12	0.90	1.15
Na_2O	9.79	9.80	6.24	6.26	8.86	10.53
SiO_2	51.97	52.02	53.09	53.28	53.65	45.84
ZrO_2	1.99	1.99	4.42	4.43	4.94	0.25
Others	5.94	5.78	7.67	7.05	4.64	12.61
Total	100.07	100.00	100.31	100.00	100.00	101.21
Waste Loading	30%		30%			

	wt% Oxide				
^{60}Co	6.2E-03	NA	1.6E-02	NA	NA
^{90}Sr	1.9E+01	NA	2.9E+01	NA	NA
^{99}Tc	3.1E-06	NA	2.0E-05	NA	NA
^{125}Sb	9.9E-02	NA	2.6E-01	NA	NA
^{134}Cs	4.4E-03	NA	<DT	NA	NA
^{137}Cs	6.0E-01	NA	2.7E-01	NA	NA
^{237}Np	4.5E-05	NA	5.7E-04	NA	NA
^{238}Pu	4.5E-05	NA	4.3E-04	NA	NA
$^{239+240}Pu$	2.4E-04	NA	4.3E-04	NA	NA
^{241}Am	3.6E-02	NA	1.0E-01	NA	NA
$^{243+244}Cm$	4.3E-04	NA	1.1E-03	NA	NA

NA = Not Added

TABLE VIII. Normalized Releases for MCC-1 28-day Leach Test (g/m^2)

	101-AZ-C1$^{(a)}$ (in-cell)	Simulant$^{(b)}$ (101-AZ-C1) (laboratory)	Model Prediction (101-AZ-C1)	101-AZ-C2$^{(a)}$ (in-cell)	Simulant$^{(b)}$ (101-AZ-C2) (laboratory)	Model Prediction (101-AZ-C2)	Sim# 3$^{(a)}$ (in-cell)	Sim# 3$^{(b)}$ (laboratory)	Model Prediction Sim# 3	ATM-10$^{(a)}$ (in-cell)	ATM-10$^{(b)(d)}$ (laboratory)
B	7.04	13.94	12.8	6.32	14.12	11.3	7.82	14.87	12.8	9.80	11.1
Li	7.10	11.78	--	6.44	11.91	--	8.08	15.50	--	9.60	11.2
Na	6.97	12.45	--	4.85	12.49	--	8.41	15.52	--	9.17	10.7
Si	6.76	10.06	--	6.16	10.03	--	8.71	12.83	--	10.40	8.39
^{60}Co	0.48			<DT							
^{90}Sr	3.4			0.83							
^{99}Tc	<DT			<DT							
^{125}Sb	5.4			8.1							
^{134}Cs	8.2			<DT							
^{137}Cs	4.9			7.2							
^{237}Np	2.4			0.53							
^{238}Pu	23.0			1.0							
$^{239+240}$Pu	6.4			7.9							
^{241}Am	0.015			0.006							
$^{243+244}$Cm	0.30			0.008							
Total U	1.2			0.32							

(a) Conducted in hot cell using fused silica-lined stainess steel containers.
(b) Conducted in laboratory using Savillex Teflon containers (9-10 threads on lids).
(c) Conducted in laboratory using fused silica-lined stainless steel containers.
(d) Data taken from Olson, K. M., Bowen, W. M., Mellinger, G. B., 1987. "MCC-1 Testing of West Valley Reference Glass--Summary Data Report." Pacific Northwest Laboratories.

<DT = below detection limits.

TABLE IX. Comparison of Leach Containers (Normalized Releases of Simulant #3)

	PCT 7-day Test				MCC-1 28-day Test		
	Laboratory			Hot Cell	Laboratory		Hot Cell
	Teflon (g/m^2)	Fused-Silica (g/m^2)	Stainless (g/m^2)	Stainless (g/m^2)	Teflon (g/m^2)	Fused-Silica (g/m^2)	Fused-Silica (g/m^2)
B	1.99	2.07	1.79	1.58	14.87	12.27	7.82
Li	1.68	1.32	1.39	1.35	15.50	11.77	8.08
Na	1.75	1.33	1.29	1.25	15.52	11.27	8.41
Si	0.49	0.45	0.42	0.47	12.83	14.02	8.71

increased instead of decreased. This is likely due to the increased silicon released from the liner as pH increases, which is over and above that accounted for by the blank. Additionally, the fused-silica sample variability was significantly greater than the Teflon. This may be attributed to variability in the durability of the liners. Comparison of the PCT leach results in the various containers shows little if any measurable difference. One would expect that the PCT results would be less affected by silicon releases from the liner, since they are minimal when compared to silicon from the glass (e.g., 2.0 μg/ml Si in the blank versus 230 [illegible]l Si in the sample).

In addition to the leach container testing, the temperature profile of the furnace was retested and the thermocouples used in the test were checked. These activities indicated a temperature gradient of 2.7°C in the oven and a thermocouple reading of 1.8°C too high, resulting in sample temperatures of 86.5°C to 89.1°C. A thermodynamic/kinetic computer model for dissolution of glass was used to estimate the effects of temperature on the MCC-1 test. Temperature effects were close to that defined by the Arrhenius' Law. Based on this and an assumed activation energy of 80kJ/mole, which is typical for this type of glass, a 3°C reduction in temperature relates to a 20% reduction in dissolution rate. A combined affect from temperature and leach container appears to account for the discrepancy in MCC-1 hot cell tests.

CONCLUSIONS

Three NCAW core samples have been characterized and treated, two of which have been vitrified into glass having acceptable properties relative to HWVP processing and waste disposal. Analysis of the pretreated waste shows that compositions are well within the design range established for HWVP with minor exceptions. Initial comparisons of waste simulants and waste simulant correlations to actual waste show good agreement in physical and rheological properties. Process offgas data from one radioactive sample and a chemically matched simulant showed considerable differences, which appear to be due to differences in chemical composition (i.e., CO_3^-, and Rh) resulting from inaccurate core sample analysis and not due to fundamental differences between simulants and actual waste. Verification of Ru concentration in the radioactive sample is in process. Comparison of durability properties of the simulant glass and model predictions to radioactive glass appear reasonable after accounting for biases experienced in the hot cell. The processing of additional core samples is planned and necessary to accomplish the testing objective, which is to confirm the validity of simulant and glass property models relative to radioactive waste.

Biases observed in leach testing of glass in the hot cell were investigated to identify the causes. Biases were attributed to temperature variations and inaccuracies in [illegible] furnace and differences in leach containers. Small temperature variations in the MCC-1 test appear to significantly affect dissolution rate of the glass. Comparison between fused-silica and Teflon containers in a 28-day MCC-1 test shows significant differences. Silica released from the fused-silica liner is significant when compared to that released from the glass. Comparisons between fused-silica, Teflon, and stainless steel containers in a PCT leach test shows little or no difference between the containers. Silica released from the fused-silica liner during a PCT test is insignificant when compared to that released from the glass.

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