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To: Terry Todd (INL)

From: Charles L. Crawford

cc: Andrew Fellinger, Stephen Sheetz, Elizabeth Hoffman, Carol Jantzen, Jarrod Crum (PNNL), James Marra, Bill Ebert (ANL), John Vienna (PNNL)

Approved by: _____
John M. Pareizs, Technical Reviewer Date

_____
Elizabeth N. Hoffman, Process Technology Programs (PTP) Manager Date

Title: Letter Report on PCT/Monolith Glass Ceramic Corrosion Tests
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Introduction

The Savannah River National Laboratory (SRNL) is collaborating with personnel from Pacific Northwest National Laboratory (PNNL) to study advanced waste form glass ceramics for immobilization of waste from Used Nuclear Fuel (UNF) separations processes. The glass ceramic waste forms take advantage of both crystalline and glassy phases where 'troublesome' elements (e.g., low solubility in glass or very long-lived) partition to highly durable ceramic phases with the remainder of elements residing in the glassy phase. The ceramic phases are tailored to create certain minerals or unique crystalline structures that can host the radionuclides by binding them in their specific crystalline network while not adversely impacting the residual glass network (Crum et al., 2011). Glass ceramics have been demonstrated using a scaled melter test performed in a pilot scale (1/4 scale) cold crucible induction melter (CCIM) (Crum et al., 2014; Maio et al., 2015). This report summarizes recent results from both Phase I and Phase II bench scale tests involving crucible fabrication and corrosion testing of glass ceramics using the Product Consistency Test (PCT). Preliminary results from both Phase I and Phase II bench scale tests involving statistically designed matrices have previously been reported (Crawford, 2013; Crawford, 2014).

Experimental

Details pertaining to the glass ceramic fabrication, durability testing via the static powdered leach testing PCT (ASTM C-1285) and analytical instrumentation have been presented in earlier reports (Crawford, 2013; Crawford, 2104).

Glass Ceramic Cesium Analyses for Phase I and Phase II Glass Ceramics

Previous studies presented the batch compositions of the Phase I and Phase II glass ceramics as well as the measured compositions except for cesium. Cesium chemical composition for both the Phase I and latter Phase II glass ceramics are shown in Table 1 and Table 2, respectively. The cesium analysis data from the dissolved glass ceramics indicates that nominally 80% of the batched cesium is recovered in the glass ceramic matrices as the Cs_2O with a standard deviation of 10 to 13%.

Phase I Glass Ceramic PCT Data

This section will present PCT leachate data that was not available during the initial reporting for the Phase I glass ceramics (Crawford, 2013). Cesium leachate data corrected for dilutions for the initial 7-day and 28-day PCTs are presented in Table 3. Appendix A shows the as-analyzed Cs leachate values in Table A-1. The normalized concentration values based on cesium are presented in Table 4 for the 7-day and 28-day PCTs. Dilution corrected leachate data for longer term 119-day and 448-day PCTs and the ambient temperature measured pHs are shown in Table 5 and Table 6, respectively. Appendix A shows the as-analyzed values in Table A-2 (119-day) and Table A-3 (448 day). Tables 7 and 8 show normalized concentrations, NC_i in units of (g glass ceramic/L) for the 119-day and 448-day tests, respectively. These data were generated using the measured chemical composition of the Phase I glass ceramic (Crawford, 2013) and the analyzed cesium values from Table 1. The NC_i equation is given below.

$$NC_i = C_i(\text{sample}) / f_i$$

where:

NC_i = normalized concentration, g waste form/L leachant,
C_i(sample) = concentration of element "i" in the solution, g_i/L,
f_i = mass fraction of element "i" in the unleached waste form (unitless).

Normalized concentrations for the glass components (B, Na and Li) as well as key waste components (Mo and Cs) are shown in Figures 1-5 for the Phase I PCT leachates. These normalized concentrations show similar trends to those from long term leach studies on glass, e.g., SON68 glass that was studied in previous work involving long term PCT leach studies from SRNL (Ebert et al., 2011).

These glass ceramic PCT tests used a polished coupon that was present along with the crushed, powdered glass ceramic matrix. A small spot of silicone adhesive was put on the coupons to mask out a small surface of pristine glass ceramic. Table 9 shows the data associated with the coupons for the Phase I tests. Adding the silicone to the coupons contributed about 11 +/- 7 mg of mass for the samples. No significant changes in mass are observed for all the samples except for the mass loss shown for the coupons O3 (average mass loss in range of 3.1 to 4.7 mg), which also shows the highest leach rates from the normalized concentration data. Leached coupons from the Phase I testing have been transferred to PNNL for analysis.

Table 1. Phase I Glass Ceramic Cesium Composition

Sample ID	Cs Analyzed Wt%	Cs_2O Analyzed Wt%	Cs_2O Target Wt%	Analyzed/ Target (%)
C1	2.64	2.80	4.85	57.8
C20	4.09	4.34	4.85	89.4
O3	3.34	3.54	4.56	77.5
O6	2.79	2.96	5.51	53.8
O8	4.95	5.25	5.69	92.3
O10	3.55	3.76	4.29	87.7
O13	4.92	5.22	5.90	88.5
I14	3.77	4.00	4.61	86.8
O15	3.75	3.97	4.36	91.1
O16	3.45	3.66	4.56	80.3
			Avg.	**80.5**
			St.Dev.	**13.8**
			%RSD	**17.1**

Table 2. Phase II Glass Ceramic Cesium Composition

Sample ID	Cs Analyzed Wt%	Cs_2O Analyzed Wt%	Cs_2O Target Wt%	Analyzed/Target (%)
O21	2.19	2.32	3.92	59.3
O23	3.35	3.55	4.00	88.6
O25	5.04	5.35	6.82	78.4
O27	5.75	6.09	6.60	92.3
I29	3.66	3.88	4.60	84.5
I31	3.90	4.14	4.44	93.3
I33	3.62	3.84	4.21	91.0
I35	3.77	3.99	5.40	74.0
I36	3.55	3.76	5.58	67.4
O22	3.11	3.29	3.85	85.6
O24	5.93	6.28	6.89	91.2
O26	5.20	5.51	6.02	91.5
O28	4.58	4.86	5.73	84.8
I30	3.98	4.22	4.53	93.2
I32	3.29	3.49	4.36	80.0
I34	2.89	3.06	4.29	71.4
O39	5.67	6.02	6.82	88.2
I40	3.48	3.69	5.58	66.1
C41	4.04	4.28	4.85	88.3
			Avg.	**82.6**
			St.Dev.	**10.4**
			%RSD	**12.6**

Table 3. Phase I Cs Dilution Corrected Leachate Concentrations for 7 and 28 Days

Sample ID	7 Day	28 Day
	mg/L	mg/L
C1	5.24	5.57
C20	10.61	11.77
O3	127.71	131.02
O6	63.20	65.67
O8	24.58	31.30
O10	5.67	6.12
O13	78.06	80.70
I14	64.72	67.42
O15	11.80	12.98
O16	2.46	2.71

Table 4. Phase I Normalized Cs Concentrations for 7 and 28 Days

Sample ID	7 Day	28 Day
	g/L	g/L
C1	0.20	0.21
C20	0.26	0.29
O3	3.83	3.93
O6	2.26	2.35
O8	0.50	0.63
O10	0.16	0.17
O13	1.59	1.64
I14	1.72	1.79
O15	0.31	0.35
O16	0.07	0.08

Table 5. Phase I Dilution Corrected Leachate Concentrations for 119 Day PCT

Sample ID	Al	B	Ba	Ca	Li	Mo	Na	Si	Sr	Te	Cs	
	(mg/L)	(mg/L)	(mg/L)	(mg/L)	(mg/L)	(mg/L)	(mg/L)	(mg/L)	(mg/L)	(mg/L)	(mg/L)	pH
Blank	<0.100	<0.100	<0.100	<0.100	<0.100	<1.00	<1.00	2.58	<0.100	<0.100	<0.020	
C1	<0.17	8.34	3.84	2.84	2.90	16.06	8.82	14.62*	2.11	<0.17	7.18	8.83
C20	0.55	10.53	3.89	2.72	2.58	22.29	11.08	11.14*	2.17	<0.17	15.03	9.14
03	6.74	387.50	2.33	1.47	104.21	358.18	575.92	190.42	1.77	15.77	147.53	10.06
06	<0.17	32.28	4.10	11.21	<0.17	45.44	82.64	49.52	4.49	1.09	68.20	9.90
08	0.64	39.77	2.10	4.70	<0.17	8.00	12.49	15.70*	2.47	0.36	44.42	8.65
010	0.88	3.63	6.57	1.97	<0.17	19.03	19.79	9.14*	2.19	<0.17	7.14	9.29
013	<0.17	56.93	3.24	4.37	22.87	41.32	<1.67	73.41	3.57	1.46	88.72	9.12
I14	<0.17	247.33	1.16	18.72	13.33	5.40	156.80	61.03	1.73	5.45	71.87	9.08
015	1.02	22.63	0.51	5.51	3.69	2.87	2.10	16.90*	0.97	<0.17	14.70	8.81
016	1.18	5.22	2.12	5.02	2.79	7.59	3.31	9.06*	1.15	<0.17	3.50	9.66

*blank Si value is > 10% of analyzed Si for these tests

Table 6. Phase I Dilution Corrected Leachate Concentrations for 448 Day PCT

Sample ID	Al	B	Ba	Ca	Li	Mo	Na	Si	Sr	Te	Cs	
	(mg/L)	(mg/L)	(mg/L)	(mg/L)	(mg/L)	(mg/L)	(mg/L)	(mg/L)	(mg/L)	(mg/L)	(mg/L)	pH
Blank	<0.100	<0.100	<0.100	<0.100	<0.100	<1.00	<1.00	13.26	<0.100	<0.100	<0.004	
C1	0.39	5.39	2.29	3.93	4.78	17.30	10.95	7.84*	<0.17	<0.17	7.93	9.29
C20	0.74	7.76	3.18	4.07	4.40	26.82	13.73	3.50*	1.87	<0.17	18.03	9.24
03	7.06	365.81	1.57	3.52	115.20	389.51	567.05	209.48	<0.17	5.63	140.39	10.13
06	<0.17	28.31	4.23	7.43	<0.17	39.22	85.75	47.61*	2.99	<0.17	71.45	10.22
08	0.71	40.15	1.15	5.51	<0.17	10.12	16.01	7.72*	1.91	<0.17	56.89	8.73
010	0.48	3.85	3.83	3.48	<0.17	26.47	25.41	5.36*	2.27	<0.17	13.73	9.65
013	0.28	48.97	3.04	6.09	22.25	47.34	2.67	69.88*	3.75	<0.17	90.19	9.46
I14	<0.17	251.63	0.17	6.23	14.46	4.46	158.04	55.33*	<0.17	1.99	70.53	9.17
015	0.94	23.87	0.17	7.97	5.52	1.88	3.19	8.12*	<0.17	<0.17	17.28	9.07
016	0.77	3.41	1.40	8.44	5.42	7.43	5.43	**	<0.17	<0.17	3.48	8.26

*blank Si value is > 10% of analyzed Si for these tests
**blank Si value higher than analyzed Si for this test

Table 7. Phase I Normalized Concentrations for 119 Day PCT

Sample ID	Al	B	Ba	Ca	Li	Mo	Na	Si	Sr	Te	Cs
	(g/L)	(g/L)	(g/L)	(g/L)	(g/L)	(g/L)	(g/L)	(g/L)	(g/L)	(g/L)	(g/L)
C1	<0.01	0.34	0.11	0.07	0.68	0.40	0.35	NA	0.14	<0.01	0.27
C20	0.02	0.39	0.12	0.07	0.62	0.57	0.44	NA	0.14	<0.01	0.37
03	3.32	11.40	0.07	0.05	12.39	7.20	10.30	1.38	0.13	0.72	4.42
06	<0.09	1.72	0.12	0.18	NA	1.92	1.95	0.34	0.26	0.04	2.44
08	0.02	1.22	0.05	0.19	NA	0.17	1.15	NA	0.15	<0.01	0.90
010	0.02	0.19	0.22	0.07	NA	0.50	0.41	NA	0.17	0.01	0.20
013	<0.08	2.01	0.08	0.18	3.11	0.84	<0.25	0.51	0.21	0.05	1.80
I14	<0.01	4.98	0.04	0.63	8.97	0.14	5.25	0.41	0.13	0.24	1.90
015	0.03	0.45	0.02	0.12	0.46	0.08	0.39	NA	0.08	<0.01	0.39
016	0.03	0.26	0.07	0.07	0.33	0.25	0.22	NA	0.08	<0.01	0.10

NA – Normalized values for Si not calculated since blank Si > 10% of analyzed Si for these tests

Table 8. Phase I Normalized Concentrations for 448 Day PCT

Sample ID	Al	B	Ba	Ca	Li	Mo	Na	Si	Sr	Te	Cs
	(g/L)	(g/L)	(g/L)	(g/L)	(g/L)	(g/L)	(g/L)	(g/L)	(g/L)	(g/L)	(g/L)
C1	0.02	0.22	0.07	0.10	1.12	0.43	0.43	NA	<0.01	0.01	0.30
C20	0.03	0.28	0.10	0.10	1.06	0.69	0.55	NA	0.12	0.01	0.44
03	3.48	10.76	0.05	0.12	13.70	7.83	10.15	1.52	<0.01	0.72	4.21
06	<0.09	1.51	0.12	0.12	NA	1.65	2.03	NA	0.17	0.04	2.56
08	0.02	1.23	0.03	0.23	NA	0.22	1.48	NA	0.11	0.01	1.15
010	0.01	0.20	0.13	0.12	NA	0.69	0.52	NA	0.17	0.01	0.39
013	0.13	1.73	0.08	0.25	3.02	0.96	0.39	NA	0.22	0.05	1.83
I14	<0.01	5.07	0.01	0.21	9.74	0.12	5.29	NA	<0.01	0.24	1.87
015	0.02	0.47	0.01	0.18	0.70	0.05	0.60	NA	<0.01	0.01	0.46
016	0.02	0.17	0.05	0.12	0.64	0.24	0.36	NA	<0.01	0.01	0.10

NA – Normalized values for Si not calculated since blank Si > 10% of analyzed Si for these tests

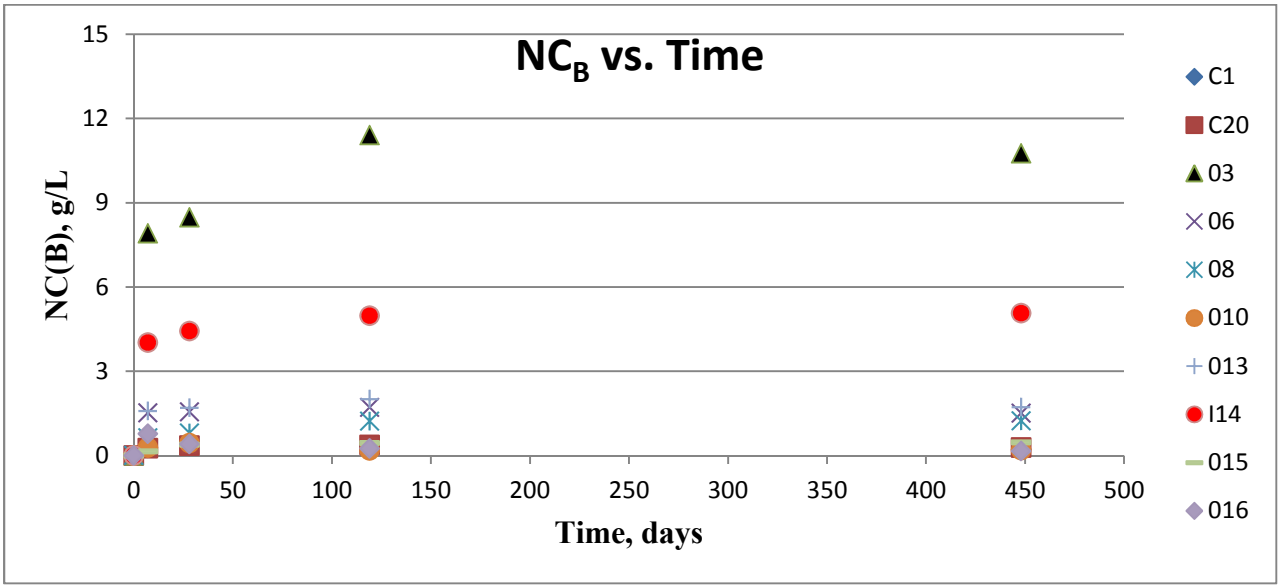

Figure 1. Phase I NC$_B$ vs. Time

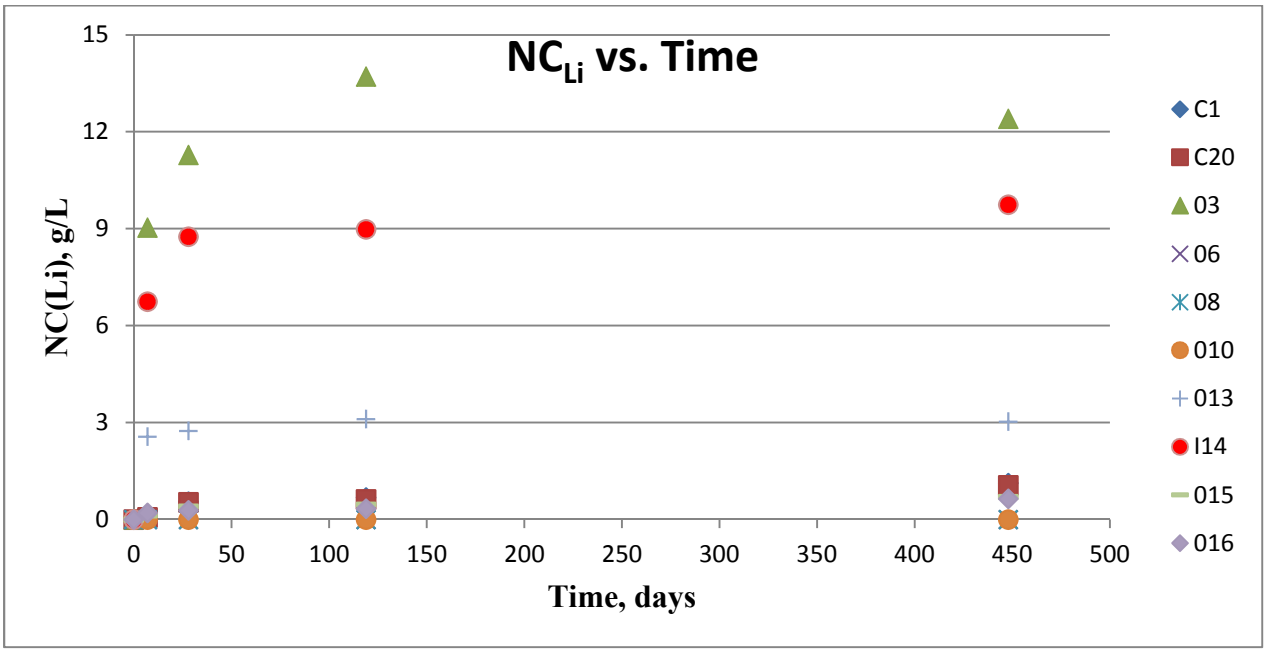

Figure 2. Phase I NC$_{Li}$ vs. Time

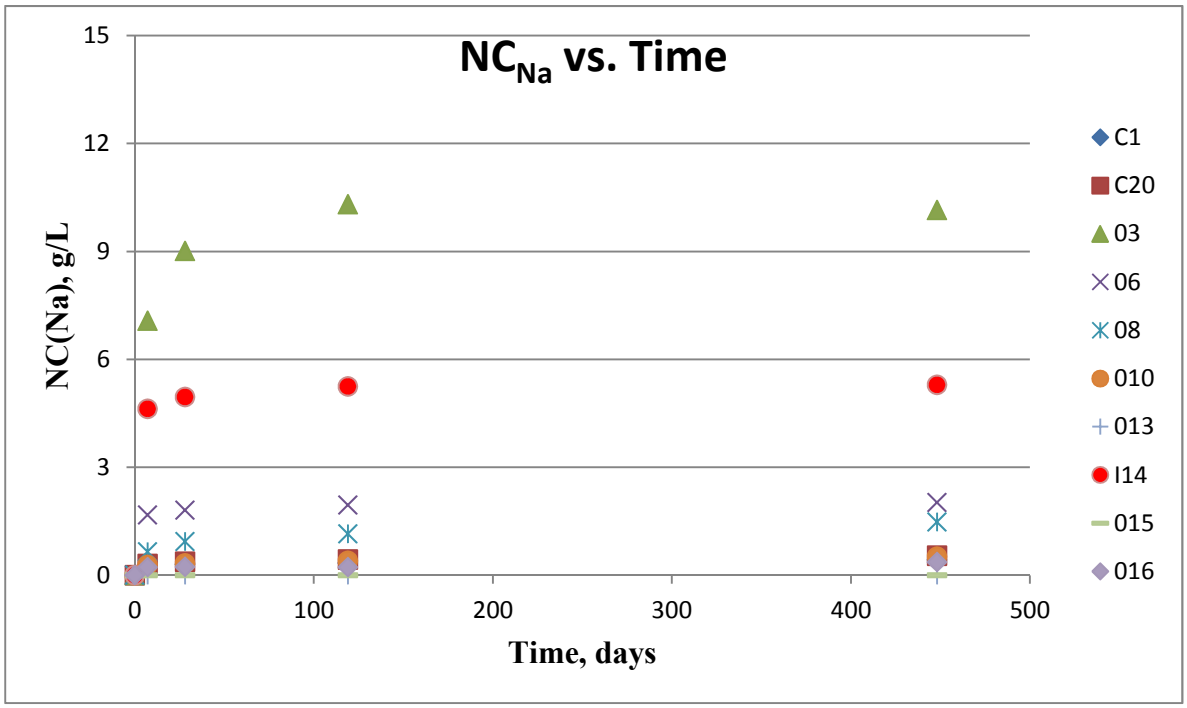

Figure 3. Phase I NC_{Na} vs. Time

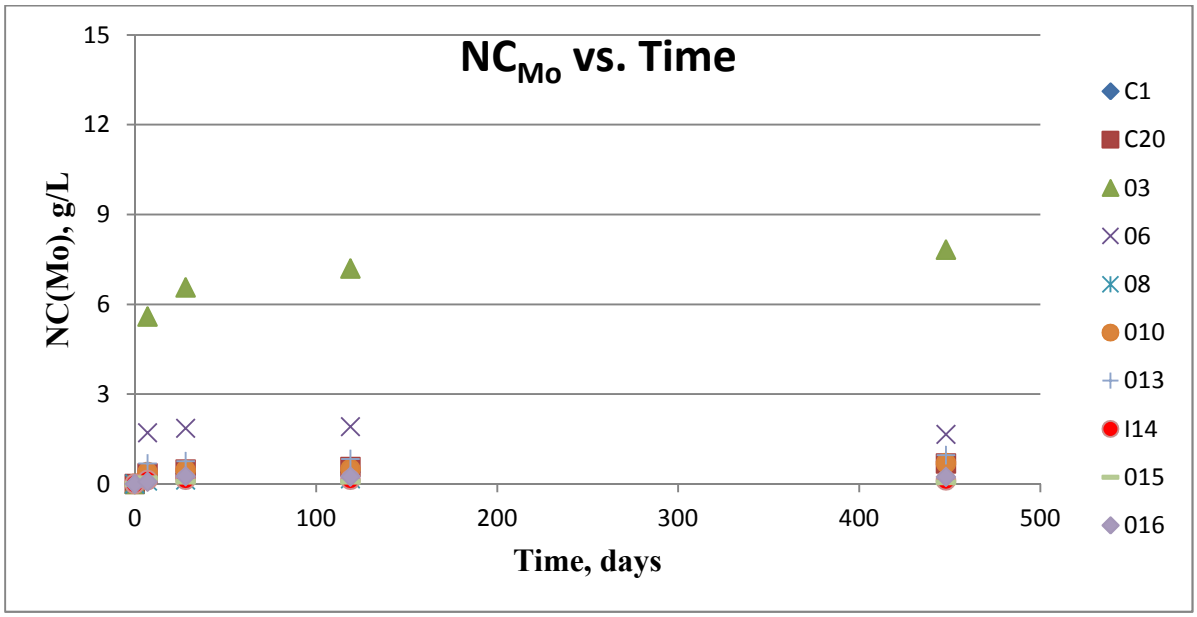

Figure 4. Phase I NC_{Mo} vs. Time

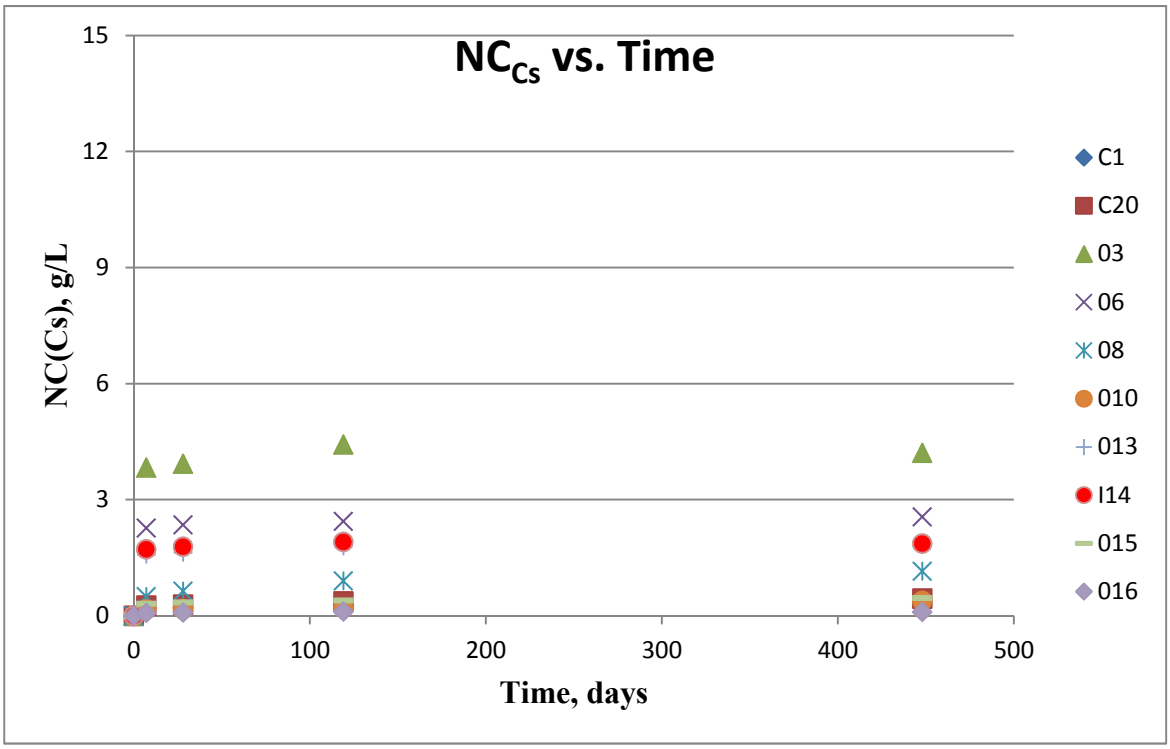

Figure 5. Phase I NC_{Cs} vs. Time

Table 9. Coupon Mass Measurements for Phase I PCT

Sample I.D.	Mass (g)	Length (mm)	Width (mm)	Thickness (mm)	Mass After Silicone (g)	Ratio Sil./No Sil.	Mass After PCT (g)	Initial - Final	Final / Initial
C1 7d	0.363	9.99	8.08	1.46	0.3659	1.008	0.366	-0.0001	1.0003
C1 28d	0.351	10.06	7.38	1.50	0.3543	1.009	0.3547	-0.0004	1.0011
C1 119d	0.35	9.94	7.34	1.56	0.3535	1.010	0.3534	0.0001	0.9997
C1 448d	0.329	9.79	7.26	1.47	0.3312	1.007	0.3312	0.0000	1.0000
C1-Coupon-5	0.33	9.79	7.34	1.46	0.3329	1.009	TBD	TBD	TBD
C20 7d	0.725	13.64	10.55	1.56 & 1.66	0.7272	1.003	0.7273	-0.0001	1.0001
C20 28d	0.653	11.82	11.18	1.66	0.6577	1.007	0.6593	-0.0016	1.0024
C20 119d	0.457	12.10	10.59	1.07 & 1.11	0.4611	1.009	0.4609	0.0002	0.9996
C20 448d	0.595	11.29	9.65	1.89	0.5997	1.008	0.5996	0.0001	0.9998
C20-Coupon-5	0.285	11.38	8.20	0.99	0.2882	1.011	TBD	TBD	TBD
03 7d	0.269	8.97	7.95	1.25	0.2732	1.016	0.2701	0.0031	0.9887
03 28d	0.286	9.01	7.72	1.35	0.2906	1.016	0.2875	0.0031	0.9893
03 119d	0.287	8.92	8.37	1.29	0.2906	1.013	0.2859	0.0047	0.9838
03 448d	0.271	9.03	7.61	1.27 & 1.30	0.2766	1.021	0.2724	0.0042	0.9848
03-Coupon-5	0.299	8.78	8.33	1.32	0.3028	1.013	TBD	TBD	TBD
06 7d	0.11	7.08	5.78	0.78	0.112	1.018	0.1121	-0.0001	1.0009
06 28d	0.098	7.07	5.82	0.72	0.1017	1.038	0.1018	-0.0001	1.0010
06 119d	0.092	6.79	5.53	0.78	0.0937	1.018	0.0935	0.0002	0.9979
06 448d	0.09	6.98	5.33	0.73	0.0921	1.023	0.0919	0.0002	0.9978
06-Coupon-5	0.099	7.00	5.34	0.73	0.1009	1.019	TBD	TBD	TBD
08 7d	0.337	10.21	8.65	1.10	0.3384	1.004	0.3385	-0.0001	1.0003
08 28d	0.357	10.12	8.64	1.19	0.3586	1.004	0.3591	-0.0005	1.0014
08 119d	0.334	9.60	8.65	1.11	0.3349	1.003	0.3348	0.0001	0.9997
08 448d	0.315	9.74	8.67	1.10	0.3171	1.007	0.317	0.0001	0.9997
08-Coupon-5	0.317	8.76	8.66	1.20 & 1.16	0.3188	1.006	TBD	TBD	TBD

Table 9. Coupon Mass Measurements for Phase I PCT, continued

Sample I.D.	Mass (g)	Length (mm)	Width (mm)	Thickness (mm)	Mass After Silicone (g)	Ratio Sil./No Sil.	Mass After PCT (g)	Initial - Final	Final / Initial
O10 7d	0.323	9.01	8.50	1.38	0.3242	1.004	0.3244	-0.0002	1.0006
O10 28d	0.295	9.12	8.33	1.30	0.2978	1.009	0.298	-0.0002	1.0007
O10 119d	0.319	9.07	8.38	1.35	0.3203	1.004	0.3199	0.0004	0.9988
O10 448d	0.167	8.02	6.05	1.27	0.1697	1.016	0.1693	0.0004	0.9976
O10-Coupon-5	0.1	5.78	4.82	1.29	0.1005	1.005	TBD	TBD	TBD
O13 7d	0.351	9.56	8.39	1.29	0.3524	1.004	0.3528	-0.0004	1.0011
O13 28d	0.323	9.24	8.12	1.28	0.3237	1.002	0.3238	-0.0001	1.0003
O13 119d	0.137	8.45	7.23	0.73	0.1399	1.021	0.139	0.0009	0.9936
O13 448d	0.155	7.28	4.58	1.30	0.157	1.013	0.1567	0.0003	0.9981
O13-Coupon-5	0.132	5.86	5.21	1.29	0.133	1.008	TBD	TBD	TBD
I14 7d	0.141	8.07	7.86	0.81 & 0.72	0.1423	1.009	0.1439	-0.0016	1.0112
I14 28d	0.216	8.66	7.62	1.09	0.217	1.005	0.2174	-0.0004	1.0018
I14 119d	0.226	8.60	7.26	1.19	0.2279	1.008	0.2278	0.0001	0.9996
I14 448d	0.246	8.56	7.41	1.23	0.2483	1.009	0.2481	0.0002	0.9992
I14-Coupon-5	0.104	6.23	5.77	1.25	0.1048	1.008	TBD	TBD	TBD
O15 7d	0.11	5.83	5.31	1.15	0.1109	1.008	0.1108	0.0001	0.9991
O15 28d	0.117	5.82	5.11	1.25	0.1187	1.015	0.1201	-0.0014	1.0118
O15 119d	0.123	5.84	5.15	1.29	0.1262	1.026	0.1262	0.0000	1.0000
O15 448d	0.097	5.30	4.96	1.13	0.0982	1.012	0.098	0.0002	0.9980
O15-Coupon-5	0.11	5.27	5.06	1.30	0.1123	1.021	TBD	TBD	TBD
O16 7d	0.336	9.59	8.17	1.40	0.3378	1.005	0.3384	-0.0006	1.0018
O16 28d	0.178	7.36	5.56	1.33	0.179	1.006	0.1797	-0.0007	1.0039
O16 119d	0.299	7.96	7.77	1.57	0.3008	1.006	0.3007	0.0001	0.9997
O16 448d	0.388	9.36	9.01	1.66	0.3901	1.005	0.389	0.0011	0.9972
O16-Coupon-5	0.262	8.70	6.73	1.56	0.2642	1.008	TBD	TBD	TBD

Phase II Glass Ceramic PCT Data

This section will present PCT leachate data that was not available during the initial reporting for the Phase II glass ceramics (Crawford, 2014). Cesium dilution corrected leachate data and normalized concentrations are shown in Table 10 for the 7-day Phase II PCT. Dilution corrected leachate data and normalized concentrations are shown in Table 11 and Table 12, respectively, for the 28-day Phase II PCT data. Cesium analysis for these 28-day leachates is currently being performed and will be reported along with ongoing longer term leach tests (16 week and 64 week durations) at a later time. As analyzed leachate data supporting these tables are shown in Appendix A, Tables A-4 and A-5.

Table 10. Phase II Cs Dilution Corrected Leachate Concentrations and Normalized Concentrations for 7 Day PCT

	Leachate	NC_{Cs}
	mg/L	g/L
O21	6.29	0.29
O23	19.08	0.57
O25	74.99	1.49
O27	13.26	0.23
I29	69.11	1.89
I31	36.73	0.94
I33	14.31	0.40
I35	89.48	2.38
I36	38.27	1.08
O22	171.71	5.53
O24	129.66	2.19
O26	30.12	0.58
O28	6.03	0.13
I30	6.00	0.15
I32	17.43	0.53
I34	33.95	1.18
O39	106.85	1.88
I40	21.58	0.62
C41	7.95	0.20

Table 11. Phase II Dilution Corrected Leachate Concentrations from 28-Day PCT*

Sample ID	Al	B	Ba	Ca	Li	Mo	Na	Si	Sr	Te
	(mg/L)	(mg/L)	(mg/L)	(mg/L)	(mg/L)	(mg/L)	(mg/L)	(mg/L)	(mg/L)	(mg/L)
O21	3.16	4.48	5.86	5.24	<1.67	16.19	24.06	9.23	3.11	1.54
O23	0.40	16.02	0.22	5.80	9.12	7.40	8.09	40.93	3.03	<0.83
O25	0.29	30.88	18.87	15.23	16.69	7.18	5.68	111.61	11.01	3.94
O27	1.53	9.03	2.10	9.45	<1.67	1.32	5.17	14.89	4.19	<0.83
I29	2.35	191.48	1.23	3.72	44.60	104.30	260.11	123.90	3.01	14.73
I31	0.28	70.86	7.13	13.73	20.21	4.77	20.34	64.68	8.51	4.88
I33	1.82	21.85	<0.17	2.93	6.16	3.50	7.91	22.94	1.98	1.00
I35	1.29	39.44	3.01	7.29	18.06	48.78	55.48	68.77	4.86	20.75
I36	0.96	16.60	3.28	7.65	4.94	33.90	37.76	36.08	4.67	6.98
O22	0.47	230.50	14.15	17.40	<1.67	15.51	128.03	122.07	9.52	6.21
O24	0.88	88.92	6.15	5.58	<1.67	35.63	142.36	125.93	10.09	3.07
O26	3.23	14.40	1.73	3.26	6.54	13.37	3.38	10.95	5.06	0.97
O28	2.50	<1.67	1.25	1.23	<1.67	3.20	4.37	12.01	1.98	<0.83
I30	2.47	2.42	<0.17	2.43	2.23	2.82	4.61	16.14	1.68	<0.83
I32	0.85	14.01	3.52	8.24	4.24	28.79	36.85	27.68	4.85	3.06
I34	1.58	23.32	1.99	1.15	8.85	63.63	42.77	34.30	2.58	4.81
O39	0.41	30.27	14.76	12.94	20.35	12.99	5.42	125.95	9.64	6.68
I40	0.90	9.47	3.31	2.26	3.36	29.06	25.24	27.41	3.44	1.96
C41	0.85	5.62	4.13	3.22	3.45	15.32	10.03	17.23	3.29	<0.83

* Cs analysis from leachates to be reported at later time

Table 12. Phase II Normalized Concentrations from 28-Day PCT*

Sample ID	Al	B	Ba	Ca	Li	Mo	Na	Si	Sr	Te
	g/L	g/L	g/L	g/L	g/L	g/L	g/L	g/L	g/L	g/L
O21	0.08	0.26	0.21	0.09	NA	1.10	0.55	0.07	0.24	0.21
O23	0.26	0.91	0.01	0.12	1.12	0.49	2.18	0.26	0.24	<0.06
O25	0.17	1.52	0.42	0.23	1.93	0.15	1.04	0.65	0.55	0.34
O27	0.05	0.26	0.05	0.15	NA	0.08	0.49	0.11	0.21	<0.07
I29	0.16	6.23	0.04	0.11	7.28	2.08	6.25	0.83	0.21	1.68
I31	0.02	2.14	0.24	0.45	3.30	0.16	1.77	0.41	0.63	0.53
I33	0.06	0.68	0.01	0.10	1.47	0.07	0.74	0.17	0.15	0.13
I35	0.09	1.93	0.08	0.14	3.12	2.08	1.85	0.49	0.30	2.07
I36	0.06	0.78	0.09	0.14	1.89	1.43	0.90	0.24	0.28	0.72
O22	0.24	7.66	0.58	0.30	NA	0.27	6.40	0.96	0.79	0.86
O24	0.73	2.46	0.14	0.20	NA	2.19	2.46	0.74	0.49	0.25
O26	0.09	0.47	0.04	0.13	0.86	0.96	0.61	0.08	0.28	0.10
O28	0.07	0.11	0.03	0.05	NA	0.06	0.45	0.08	0.11	<0.12
I30	0.08	0.12	0.01	0.05	0.82	0.05	0.40	0.10	0.12	<0.11
I32	0.06	0.73	0.10	0.15	1.67	1.25	0.89	0.19	0.28	0.34
I34	0.12	1.14	0.07	0.05	1.96	1.44	1.09	0.26	0.18	0.62
O39	0.19	1.72	0.32	0.20	2.47	0.18	0.84	0.80	0.46	0.60
I40	0.07	0.50	0.12	0.07	1.37	1.09	0.69	0.18	0.25	0.26
C41	0.04	0.23	0.13	0.09	0.81	0.37	0.42	0.12	0.22	<0.10

* Cs analysis from leachates to be reported at later time
NA – No Li was added to these glass ceramics

Phase I and Phase II 7-day PCT Test Results

The 7-day PCT static leach test is best applied towards comparison of many different glasses or in this case many different glass ceramics that derive from statistically designed compositions. Comparison of the normalized concentrations from these Phase I and Phase II tests are shown in Table 13 for NC_B and NC_{Na} in units of g/L. Normalized release data for the Phase I glass ceramics are taken from Table 3 of Crawford, 2013. Normalized release for the Phase II glass ceramics are calculated from the PCT leachate concentrations and the analyzed elemental Na and B compositions in the glass ceramics. These analyzed elemental composition data were originally presented in Crawford, 2014. The data are grouped showing NC_i values in four broad ranges from lowest (up to 0.5 g/L), from >0.5 to 1.0 g/L, from >1.0 to 3.0 g/L and those above 3.0 g/L. All of these values can be compared to the Environmental Assessment (EA) glass (Jantzen et al., 1993) mentioned in the Department of Energy (DOE) Waste Acceptance Specifications (WAPS, 2012 for Vitrified High-Level Waste (HLW)) as an upper limit benchmark glass. The normalized concentrations for EA boron and sodium release are 16.695 +/- 1.222 g/L and 13.346 +/- 0.902 g/L, respectively. Direct comparison of the durability of glass ceramics and nominal HLW glass should be made on a normalized loss, NL_i, (g/m^2) basis since the glass ceramics have slightly higher densities in the range of 3.34 to 3.56 g/cc vs. nominal 2.7 g/cc for HLW glass (ASTM C-1285). The density of select glass ceramic samples were measured using the buoyancy method and are presented in Table 14 vs. a reference National Institute of Standards and Technology (NIST) glass density standard of 2.5487 g/cc. This results in lower surface area for an equivalent mass of 100 to 200 mesh powder. Equations involved in the conversions are shown below involving the surface area (SA). These data show that for a gram of 100-200 mesh glass powder, the surface area is estimated to be 1.99E-02 m^2, whereas for an equivalent gram of glass ceramic the estimated surface area is 1.56E-02m^2. Normalized B and Na concentration data from Table 13 are shown in terms of normalized release (NL_i) in Table 15 along with the NL_B and NL_{Na} values for EA glass in units of g/m^2. These data show that the normalized release values for B and Na from both Phase I and Phase II glass ceramics are all below those of EA glass.

$$NC_i = C_i / f_i, \quad g\ glass/L$$
$$NL_i = NC_i / SA/V, \quad g\ glass/m^2$$

$$SA = (6 \times \text{mass}) / \rho * d$$

100/200 mesh, 112 µm = estimate of mean diameter of particle

Nominal HLW glass density = 2.7 g/cm³
Nominal Glass Ceramic density = 3.4 g/cm³ (3.34 – 3.56)

SA_{glass} = 1.99E-02 m^2 ; $SA_{glass\ ceramic}$ = 1.56E-02 m^2

Table 13. Comparison of Normalized Concentration from 7-Day PCT for Phase I and Phase II Glass Ceramics

Phase I	Na		B		Phase II	Na		B
Sample ID	(g/L)	Sample ID	(g/L)		Sample ID	(g/L)	Sample ID	(g/L)
O16	0.23	O15	0.16		I30	0.19	O28	0.12
O13	0.25	C20	0.27		O28	0.25	I30	0.14
C1	0.27	C1	0.28		O27	0.27	O27	0.18
O10	0.29	O10	0.29		O26	0.30	O21	0.18
C20	0.32				C41	0.33	C41	0.21
-	-				O21	0.42	O26	0.42
-	-				I33	0.50		
O15	0.52	O8	0.63		I40	0.67	I40	0.51
O8	0.65	O16	0.79		O39	0.81	I33	0.53
					O25	0.87	O23	0.56
					I36	0.87	I36	0.68
					I32	0.92	I32	0.73
					O23	0.96	I34	0.99
O6	1.68	O6	1.52		I34	1.13	O25	1.21
		O13	1.58		I31	1.59	O39	1.61
					I35	2.00	I31	1.68
					O24	2.37	I35	1.76
							O24	1.91
I14	4.63	I14	4.02		I29	5.46	I29	4.99
O3	7.07	O3	7.91		O22	5.86	O22	5.49

Table 14. Glass Ceramic Measured Densities

Sample ID	Measured Density (g/cc)
I-30	3.3412, 3.3456, 3.3456
O-28	3.5628, 3.5643, 3.5643
C-41	3.3850, 3.3849
NIST 1826 Glass	2.5484, 2.5498

Table 15. Comparison of Normalized Release from 7-Day PCT for Phase I and Phase II Glass Ceramics

Phase I Sample ID	Na (g/m^2)	Sample ID	B (g/m^2)	Phase II Sample ID	Na (g/m^2)	Sample ID	B (g/m^2)
016	0.15	015	0.10	I30	0.12	O28	0.08
013	0.16	C20	0.17	O28	0.16	I30	0.09
C1	0.17	C1	0.18	O27	0.17	O27	0.11
010	0.19	010	0.18	O26	0.19	O21	0.11
C20	0.20	08	0.41	C41	0.21	C41	0.14
015	0.34	016	0.50	O21	0.27	O26	0.27
08	0.42	06	0.97	I33	0.32	I40	0.33
06	1.08	013	1.01	I40	0.43	I33	0.34
I14	2.97	I14	2.58	O39	0.52	O23	0.36
03	4.53	03	5.07	O25	0.56	I36	0.44
				I36	0.56	I32	0.47
				I32	0.59	I34	0.63
				O23	0.62	O25	0.77
				I34	0.72	O39	1.03
				I31	1.02	I31	1.07
				I35	1.28	I35	1.13
				O24	1.52	O24	1.22
				I29	3.50	I29	3.20
				O22	3.76	O22	3.52

NL_B and NL_{Na} for EA glass are 8.39 ± 0.61 g/m^2 and 6.71 ± 0.45 g/m^2 , respectively

Conclusions and Ongoing Testing

SRNL has successfully performed short and long term durability leach tests on Phase I and Phase II glass ceramics that were fabricated at both PNNL and SRNL. In the Phase I tests that used a polished coupon in addition to the standard ratios of glass powder to leachant, only one matrix showed measurable mass loss from the coupon. This O3 formulation showed the highest PCT elemental release of all the various samples tested. Long term corrosion tests performed through 448-day duration indicate that the Phase I glass ceramics behave similar to durable HLW glasses. Leachate data indicates an early 'stage I' initial release, followed by a gradual slowing of release to some 'stage II' residual rate over time. Ongoing similar tests with the Phase II glass ceramics will also be completed out through 448-day duration. Overall comparison of the 7-day PCT results of the glass ceramics vs. the EA benchmark glass indicate lower glass ceramic normalized releases for the glass ceramics than for EA glass.

A single set of samples remain for the Phase I glass ceramics that are planned for analysis at approximately the 2-year duration in early calendar year 2016. Further tests with the Phase II glass ceramics will involve 16-week and 64-week sample sets for analysis planned for late September 2015 and mid-August of 2016, respectively. A final sample set will also be available for the Phase II to be removed at the 2-year duration in May of 2017.

The 7-day PCT data from both Phase I and Phase II will be analyzed using statistical methods, e.g., JMP™ Pro, Ver. 11.2.1, [Computer Software], with respect to the chemical composition for the Phase I and Phase II glass ceramics to determine if any correlations in durability can be made with either the glass former elements (Al, B, Ca, Na, Li, Si) and/or the simulated waste elements.

SRNL will support ongoing glass ceramic formulation and process development by performing analysis on samples from bench scale and melter testing. Analyses to be performed include chemical composition measurement and corrosion testing.

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Appendix A

Glass Ceramic Composition, Analyses and PCT Leachate Data

Table A-1. Phase I Cs As-Analyzed Leachate Concentrations for 7 and 28 Days

Sample ID	7 Day	28 Day
	mg/L	mg/L
C1	3.15	3.34
C20	6.37	7.06
O3	76.63	78.61
O6	37.92	39.40
O8	14.75	18.78
O10	3.40	3.67
O13	46.84	48.42
I14	38.83	40.45
O15	7.08	7.79
O16	1.48	1.63

Table A-2. Phase I As-Analyzed Leachate Concentrations for 119 Day PCT

Sample ID	Al	B	Ba	Ca	Li	Mo	Na	Si	Sr	Te	Cs
	(mg/L)	(mg/L)	(mg/L)	(mg/L)	(mg/L)	(mg/L)	(mg/L)	(mg/L)	(mg/L)	(mg/L)	(mg/L)
Blank	<0.100	<0.100	<0.100	<0.100	<0.100	<1.00	<1.00	2.58	<0.100	<0.100	<0.020
C1	<0.10	5.00	2.31	1.71	1.74	9.64	5.29	10.32	1.27	<0.10	4.31
C20	0.33	6.32	2.33	1.63	1.55	13.37	6.65	8.23	1.30	<0.10	9.02
03	4.05	232.50	1.40	0.88	62.52	214.91	345.55	115.80	1.06	9.46	88.52
06	<0.10	19.37	2.46	6.73	<0.10	27.27	49.58	31.26	2.69	0.66	40.92
08	0.38	23.86	1.26	2.82	<0.10	4.80	7.50	10.97	1.48	0.21	26.65
010	0.53	2.18	3.94	1.18	<0.10	11.42	11.87	7.03	1.31	<0.10	4.29
013	<0.10	34.16	1.94	2.62	13.72	24.79	<1.00	45.60	2.14	0.87	53.23
I14	<0.10	148.40	0.70	11.23	8.00	3.24	94.08	38.17	1.04	3.27	43.12
015	0.61	13.58	0.31	3.30	2.21	1.72	1.26	11.69	0.58	<0.10	8.82
016	0.71	3.13	1.27	3.01	1.67	4.55	1.99	6.99	0.69	<0.10	2.10

Table A-3. Phase I As-Analyzed Leachate Concentrations for 448 Day PCT

Sample ID	Al	B	Ba	Ca	Li	Mo	Na	Si	Sr	Te	Cs
	(mg/L)	(mg/L)	(mg/L)	(mg/L)	(mg/L)	(mg/L)	(mg/L)	(mg/L)	(mg/L)	(mg/L)	(mg/L)
Blank	<0.100	<0.100	<0.100	<0.100	<0.100	<1.00	<1.00	13.26	<0.100	<0.100	<0.004
C1	0.24	3.24	1.37	2.36	2.87	10.38	6.57	12.66	<0.10	<0.10	4.76
C20	0.44	4.66	1.91	2.44	2.64	16.09	8.24	10.06	1.12	<0.10	10.82
03	4.23	219.49	0.94	2.11	69.12	233.70	340.23	133.65	<0.10	3.38	84.23
06	0.10	16.99	2.54	4.46	<0.10	23.53	51.45	36.52	1.80	<0.10	42.87
08	0.43	24.09	0.69	3.31	<0.10	6.07	9.61	12.59	1.15	<0.10	34.13
010	0.29	2.31	2.30	2.09	<0.10	15.88	15.24	11.17	1.36	<0.10	8.24
013	0.17	29.38	1.82	3.65	13.35	28.40	1.60	49.88	2.25	<0.10	54.11
I14	0.10	150.98	0.10	3.74	8.68	2.68	94.82	41.16	<0.10	1.19	42.32
015	0.57	14.32	0.10	4.78	3.31	1.13	1.91	12.83	<0.10	<0.10	10.37
016	0.46	2.05	0.84	5.06	3.25	4.46	3.26	7.20	<0.10	<0.10	2.09

Table A-4. Phase II As-analyzed Leachate Concentrations for Cs from 7-Day PCT

Sample ID	Cs	Sample ID	Cs
	(mg/L)	(mg/L)	(mg/L)
O21	3.77	O24	77.80
O23	11.45	O26	18.07
O25	44.99	O28	3.62
O27	7.96	I30	3.60
I29	41.47	I32	10.46
I31	22.04	I34	20.37
I33	8.58	O39	64.11
I35	53.69	I40	12.95
I36	22.96	C41	4.77
O22	103.03		

Table A-5. Phase II As-analyzed Leachate Concentrations and pH from 28-Day PCT*

Sample ID	Al	B	Ba	Ca	Li	Mo	Na	Si	Sr	Te	pH
	(mg/L)	(mg/L)	(mg/L)	(mg/L)	(mg/L)	(mg/L)	(mg/L)	(mg/L)	(mg/L)	(mg/L)	
Blank-1	<0.100	<1.00	<0.100	<0.100	<1.00	<0.100	1.52	<1.00	<1.00	<0.50	6.89
O21	1.89	2.69	3.52	3.15	<1.00	9.71	14.44	5.54	1.87	0.92	10.08
O23	0.24	9.61	0.13	3.48	5.47	4.44	4.86	24.56	1.82	<0.50	9.51
O25	0.17	18.53	11.32	9.14	10.02	4.31	3.41	66.97	6.61	2.37	9.59
O27	0.92	5.42	1.26	5.67	<1.00	0.79	3.10	8.94	2.51	<0.50	9.26
I29	1.41	114.89	0.74	2.23	26.76	62.58	156.07	74.34	1.81	8.84	9.46
I31	0.17	42.52	4.28	8.24	12.13	2.86	12.20	38.81	5.11	2.93	9.14
I33	1.09	13.11	<0.10	1.76	3.70	2.10	4.75	13.76	1.19	0.60	8.95
I35	0.77	23.66	1.80	4.37	10.84	29.27	33.29	41.26	2.92	12.45	9.97
I36	0.57	9.96	1.97	4.59	2.97	20.34	22.66	21.65	2.80	4.19	9.80
O22	0.28	138.30	8.49	10.44	<1.00	9.31	76.82	73.24	5.71	3.72	8.86
O24	0.53	53.35	3.69	3.35	<1.00	21.38	85.41	75.56	6.06	1.84	9.45
O26	1.94	8.64	1.04	1.95	3.93	8.02	2.03	6.57	3.04	0.58	9.18
O28	1.50	<1.00	0.75	0.74	<1.00	1.92	2.62	7.21	1.19	<0.50	8.56
I30	1.48	1.45	<0.10	1.46	1.34	1.69	2.76	9.68	1.01	<0.50	8.85
I32	0.51	8.40	2.11	4.94	2.55	17.28	22.11	16.61	2.91	1.84	10.05
I34	0.95	13.99	1.19	0.69	5.31	38.18	25.66	20.58	1.55	2.89	9.55
O39	0.25	18.16	8.86	7.76	12.21	7.79	3.25	75.57	5.78	4.01	9.65
I40	0.54	5.68	1.99	1.36	2.01	17.44	15.14	16.45	2.06	1.17	9.47
C41	0.51	3.37	2.48	1.93	2.07	9.19	6.02	10.34	1.97	<0.50	9.40

* Cs analysis from leachates to be reported at later time