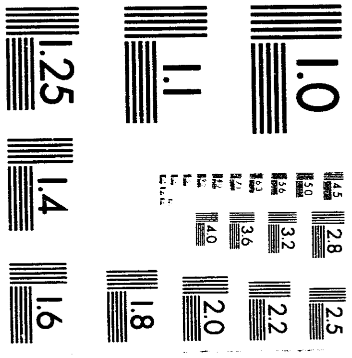
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PRODUCTION AND REMEDIATION OF LOW SLUDGE SIMULATED PUREX WASTE GLASSES, II: EFFECTS OF SLUDGE OXIDE ADDITIONS ON GLASS DURABILITY (U)

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Production of and Remediation of Low-Sludge, Simulated Purex Waste Glasses, II: Effects of Sludge Oxide Additions On Glass Durability (U)

Introduction and Summary

Glass produced during the Purex 4 campaigns of the Integrated DWPF Melter System (IDMS)[1] and the 774 Research Melter[2] contained a lower fraction of sludge components than targeted by the Product Composition Control System (PCCS).[3] Purex 4 glass was more durable than the benchmark (EA) glass, but was less durable than most other simulated SRS high-level waste glasses.[1,2,4] Further, the measured durability of Purex 4 glass was not as well correlated with the durability predicted from the DWPF process control alogrithm,[4] probably because the algorithm was developed to predict the durability of SRS high-level waste glasses with higher sludge content than Purex 4.[5]

A melter run, designated Purex 4 Remediation, was performed using the 774 Research Melter to determine if the initial PCCS target composition determined for Purex 4 would produce acceptable glass whose durability could be accurately modeled by the DWPF glass durability algorithm.[6] Reagent grade oxides and carbonates were added to Purex 4 melter feed stock to simulate a higher sludge loading. Each canister of glass produced was sampled and the glass durability was determined by the Product Consistency Test method. This document details the durability data and subsequent analysis.

The melter heel composition was a low sludge glass which was determined to be less durable than the Environmental Assessment (EA) glass. The glasses produced by adding the Purex 4 melter feed doped with sludge oxides to this heel were significantly more durable than the EA glass. The DWPF glass durability algorithm accurately models the durability of all glass produced during the Purex 4 Remediation campaign.

Background and Objectives

A series of melter campaigns designated as Purex 4 were performed by SRTC as a validation exercise for the Nitric Acid flowsheet. Purex 4 feed was successfully processed during one campaign of the IDMS[1] and three campaigns of the 774 Research Melter[2]. Purex 4 glass was demonstrated to be more durable than the EA glass standard set for Waste Acceptance.[1,6,7] However, the durability of Purex 4 glass decreased as a function of time.[1,2] Glass poured during the initial portion of the run (a combination of melter heel and Purex 4 feed) was substantially more durable than glass poured at the end of the run (composition dominated by Purex 4 feed).[1,2] Further, the measured boron release was significantly higher than predicted by the glass durability algorithm developed for Defense Waste Processing Facility (DWPF) operation.[4]

Purex 4 melter feed was considerably lower in sludge than targeted by the Product Composition Control System (PCCS) which will be used to control DWPF operation.[3,8] As a result, the blend of frit, sludge, and Precipitate Hydrolysis Aqueous (PHA) was unlike common SRS waste glass formulations. DWPF design basis sludge loading is 28 weight percent (dry solids basis).[6] The Purex 4 target blend determined by PCCS was 24.3% sludge.[3] The final Purex 4 blend actually achieved was determined to be approximately 20% sludge.[5]

Analyses performed on Purex 4 glass indicated the presence of glass-in-glass phase separation.[9] Phase separation is a phenomena that occurs whenever a combination of phases is more thermodynamically stable than a single homogeneous phase. Glass-in-glass is a term used if both phases are amorphous. One of the phases was predominately silica. The other phase consisted of the remaining silica and the other glass oxides. This multiple phase glass was considerably less durable than the DWPF durability algorithm predicted. This algorithm, referred to as the Hydration Thermodynamic model, was developed to predict the relative durability of homogeneous, single phase glasses.[10] The simulated high-level waste glasses tested to develop this model contained between 25% and 35% sludge.[10] As indicated by the Purex 4 glass, DWPF glass that is significantly depleted in sludge may also be inhomogeneous. The durability of low sludge, inhomogeneous glasses cannot at this time be controlled to the same degree as glasses previously produced at SRS. SRTC has begun investigations concerning low sludge glasses, but composition-property correlations are not currently available for these glasses.[11]

Tests were performed to determine if the Purex 4 melter feed composition could be successfully remediated to yield a homogeneous, single phase glass upon melting. A sample of Purex 4 melter feed was doped with reagent chemicals to simulate a higher sludge loading. The remediated melter feed was successfully processed into glass by the 774 Research Melter. This campaign, referred to as Purex 4 Remediation, is described elsewhere.[5] This report details the durability of glass produced during the Purex 4 Remediation campaign. The relationship between measured glass durability and the durability predicted by the Hydration Thermodynamics model is discussed.

Experimental

The Product Consistency Test (PCT) was performed on glass samples from each of the ten canisters produced during the Purex 4 Remediation campaign. Glass samples from the two canisters poured immediately prior to initiation of the Purex 4 Remediation campaign were also tested. PCT analyses were performed by D. C. Beam and L. L. Cotney. Test conditions were consistent with PCT version B.[12] PCT Leachates were submitted to the Analytical

Development Section of SRTC for analysis by Inductively Coupled Plasma - Atomic Emission Spectroscopy (B, Si, Na, Li, Al, Fe, Mn, Mg, Ca, Ni) and Atomic Absorption (Na, K). All PCT test data are maintained by D. C. Beam in notebook WSRC-NB-91-200.

The sodium and boron concentrations of the leachates were used to quantify the durability of the glasses. The sodium and boron concentrations of the glass leachates are given in Appendix 1. In addition, the relative durability (Normalized Loss, $NL_{[i]}$) of each glass was determined. Normalized Loss is calculated in the following manner:

$$NL_{[i]} \equiv \frac{ppm_{[i]_{aq}}}{(1000)f_{[i]_{glass}}}$$

where,

$ppm_{[i]}$ ⇒ concentration of element i in leachate,
$f_{[i]}$ ⇒ fraction of element i in the glass.

By placing the factor 1000 in the denominator, the units of $NL_{[i]}$ become grams of glass dissolved per liter of solution, g/L. PCT protocol requires 10 milliliters of deionized water per gram of glass. Therefore, an $NL_{[i]} = 100$ indicates the glass has completely reacted; an $NL_{[i]} = 10$ indicates 10 percent of the glass has reacted; an $NL_{[i]} = 1$ indicates 1 percent of the glass has reacted, and so on. Appendix 2 contains the Purex 4 Remediation glass compositions tested. Appendix 2 also contains the Free Energy of Hydration calculated for each glass. This calculation was done with a spreadsheet developed by C. M. Jantzen and adapted by C. A. Cicero.

Results and Discussion

The glass in the 774 Research Melter at the start of the Purex 4 Remediation campaign was a low sludge composition. This glass is best represented by the two canisters which were poured immediately prior to the Purex 4 Remediation campaign. Addition of the higher sludge Purex 4 Remediation feed significantly improved glass durability. Figure 1A illustrates the variation in glass durability (as determined by sodium release) observed as the Purex 4 Remediation feed was added to the existing melter heel. The sodium concentration in the PCT leachate from canister #1 glass was less than one-fourth that found in the previous two canisters (≅290ppm Na versus >1200ppm Na). PCT leachates from the subsequent canisters had a consistent Na concentration of approximately 130-180ppm. A similar trend is demonstrated by the boron release. The boron concentration in the PCT leachate from canister #1 glass was less than one-fourth that of the preceding canisters (100ppm vs >400ppm). The subsequent cans had still lower boron release values (50-80ppm). Figure 1B is a plot of the B release from these glasses.

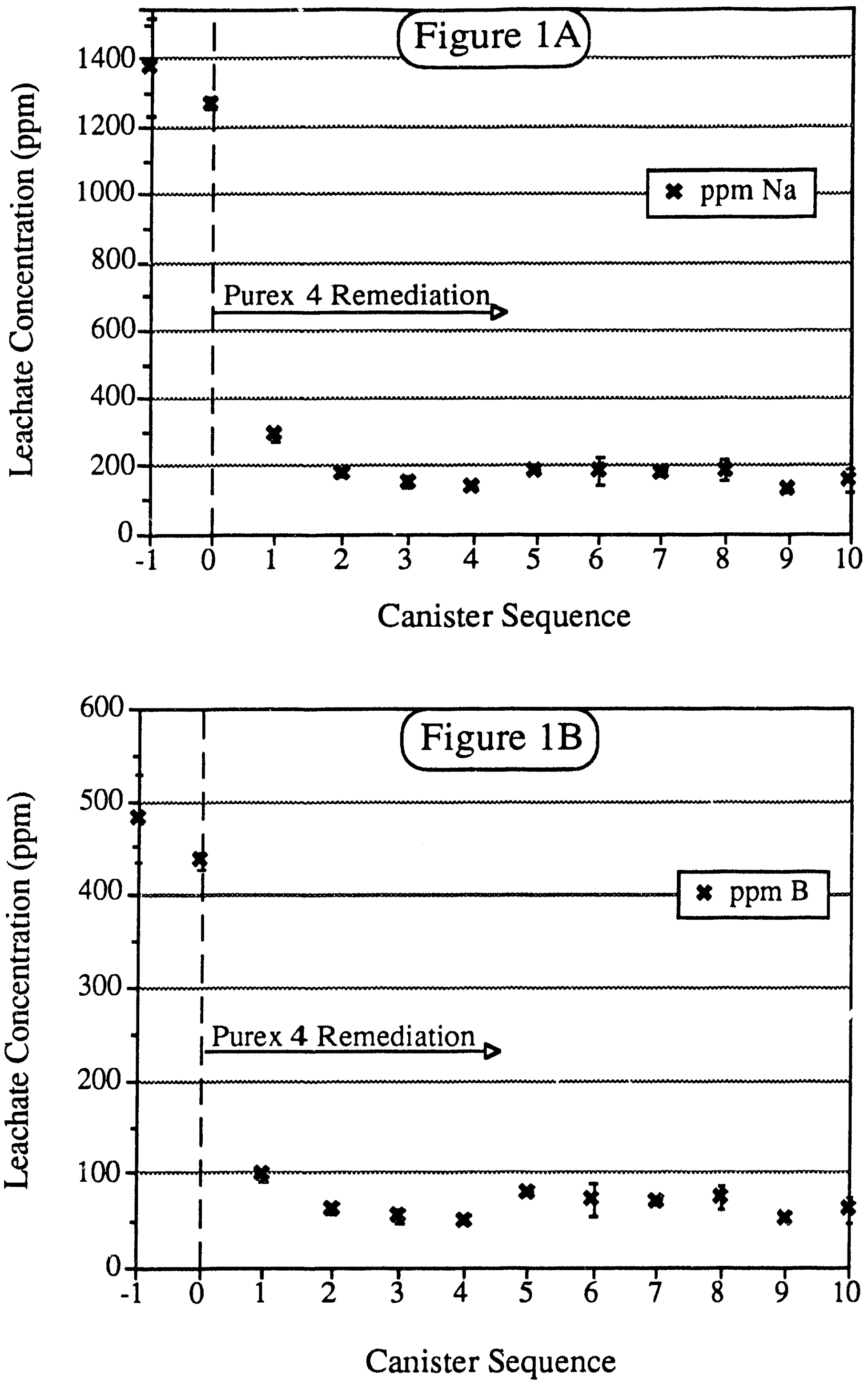

Figure 1. Durability of Glasses Produced Immediately Prior to and During the Purex 4 Remediation Campaign.

The large improvement in glass durability upon addition of the remediated Purex 4 feed to the low sludge melter heel demonstrates the importance of sludge loading in the consistent production of acceptable DWPF product. The Waste Acceptance criteria for high-level waste glass is based on the durability of the SRS EA glass.[6,7,13] Acceptable glasses have a durability greater than the EA glass (i.e. lower Normalized Release values) by two standard deviations.[6] Both canisters of low sludge glass fail to meet the Waste Acceptance criteria, i.e. would be considered an unacceptable product. All ten canisters of Purex 4 Remediation glass would be acceptable. Figure 2 is a plot of the relative glass durability (as Normalized Loss of boron, $NL_{[B]}$) as a function of canister sequence. The heavy solid line represents two standard deviations below the $NL_{[B]}$ of the EA glass.[7,13] The four-fold improvement in glass durability between canister #1 of the Purex 4 Remediation campaign and the low-sludge glasses places canister #1 well below the EA limit. Canister #1, the least durable glass of the campaign, had less than one-fourth the $NL_{[B]}$ of the EA glass.

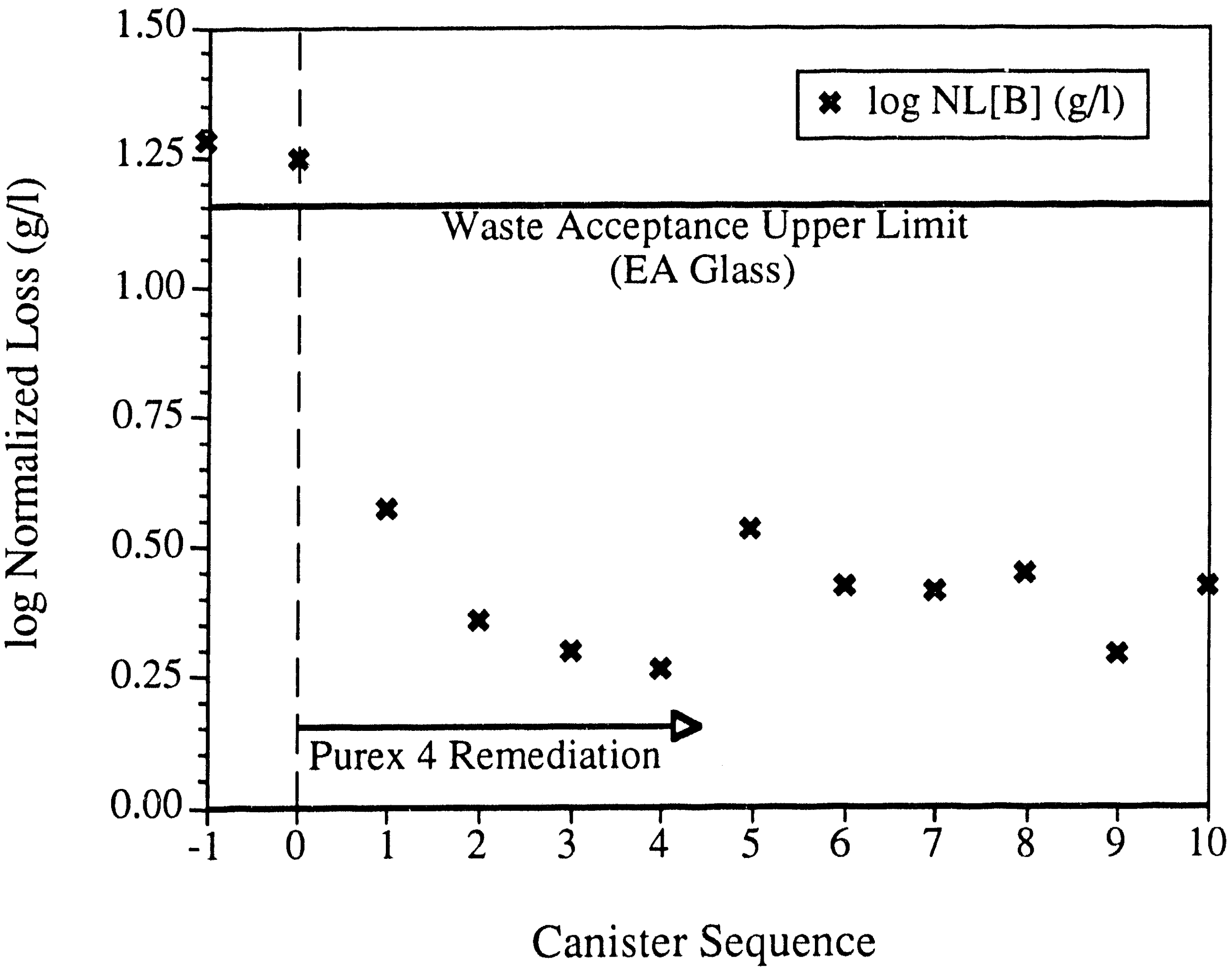

Figure 2. Comparison Between Purex 4 Remediation Glass Durability and Waste Acceptance Limit.

The significant improvement in glass durability upon addition of the remediated Purex 4 feed to the low sludge melter heel also impacts DWPF process control strategy. As mentioned earlier, the low-sludge, non-remediated Purex 4 glass was considerably less durable than predicted by the DWPF durability algorithm (the Hydration Thermodynamic model[1]).[4] The low-sludge glasses produced prior to the Purex 4 Remediation campaign are also less durable than predicted by Hydration Thermodynamics. This is demonstrated in Figure 3, a plot of the normalized loss of sodium versus the Free Energy of Hydration (ΔG_{hyd}) calculated for each glass. Included in Figure 3 are the data used to generate the Hydration Thermodynamic algorithm (denoted CMJ [Na]) as well as data for all of the Purex 4 Remediation glasses. The two low sludge melter heel glasses have similar ΔG_{hyd} values as the other Purex 4 glasses ($\cong$-7 kcal/mole). Their durability, however, is much closer to that of the EA glass, which has a $\Delta G_{hyd} \cong -10$ kcal/mole. As the EA glass represents the durability limit, this is an unacceptable relationship for process control. The durability of the Purex 4 Remediation glasses is in much better agreement with the algorithm predictions. These glasses have $-6 > \Delta G_{hyd} > -12$ kcal/mole and $0.6 > \log_{10} NL_{[Na]} > 0.2$ g/L values. These values are much more consistent with other SRS simulated high-level waste glasses.

In summary, the durability of the low sludge glasses was not well correlated with the Hydration Thermodynamic algorithm. However, the glass produced by adding the higher sludge loading Purex 4 Remediation feed to this heel was acceptable and was demonstrated to be in better agreement with the DWPF algorithm. These data confirm that control of the DWPF process using Hydration Thermodynamics is viable for glasses with sludge loading greater than $\cong$24%, which is the expected minimum sludge loading during DWPF operation. Below this sludge loading, the current algorithm is not appropriate for control.

Conclusions

The low-sludge glasses indicative of the melter heel prior to the Purex 4 Remediation campaign were less durable than the EA glass. However, adding the remediated Purex 4 feed with its higher sludge content to this heel significantly improved glass durability. All of the Purex 4 Remediation glasses were more than 5 times as durable as the EA glass. Further analysis demonstrated good agreement between Purex 4 Remediation glass durability (as determined by the PCT) and the Hydration Thermodynamic algorithm developed for the DWPF process. This study indicates that control of the DWPF process will be better achieved by maintaining sludge loading greater than or equal to approximately 24 percent.

Future Work

Additional studies are underway to determine the lowest Purex sludge concentration allowable for DWPF process control. These studies will be detailed in the report - Production and Remediation of Low-Sludge, Simulated Purex Waste Glasses, III: Effect of Sludge Concentration on Glass Production and Durability.

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[1] Since the non-remediatied Purex 4 campaigns, the Hydration Thermodynamic algorithm has been updated to model PCT results.[9] The calculations and graph (Figure 3) used in this report are based on this updated algorithm.

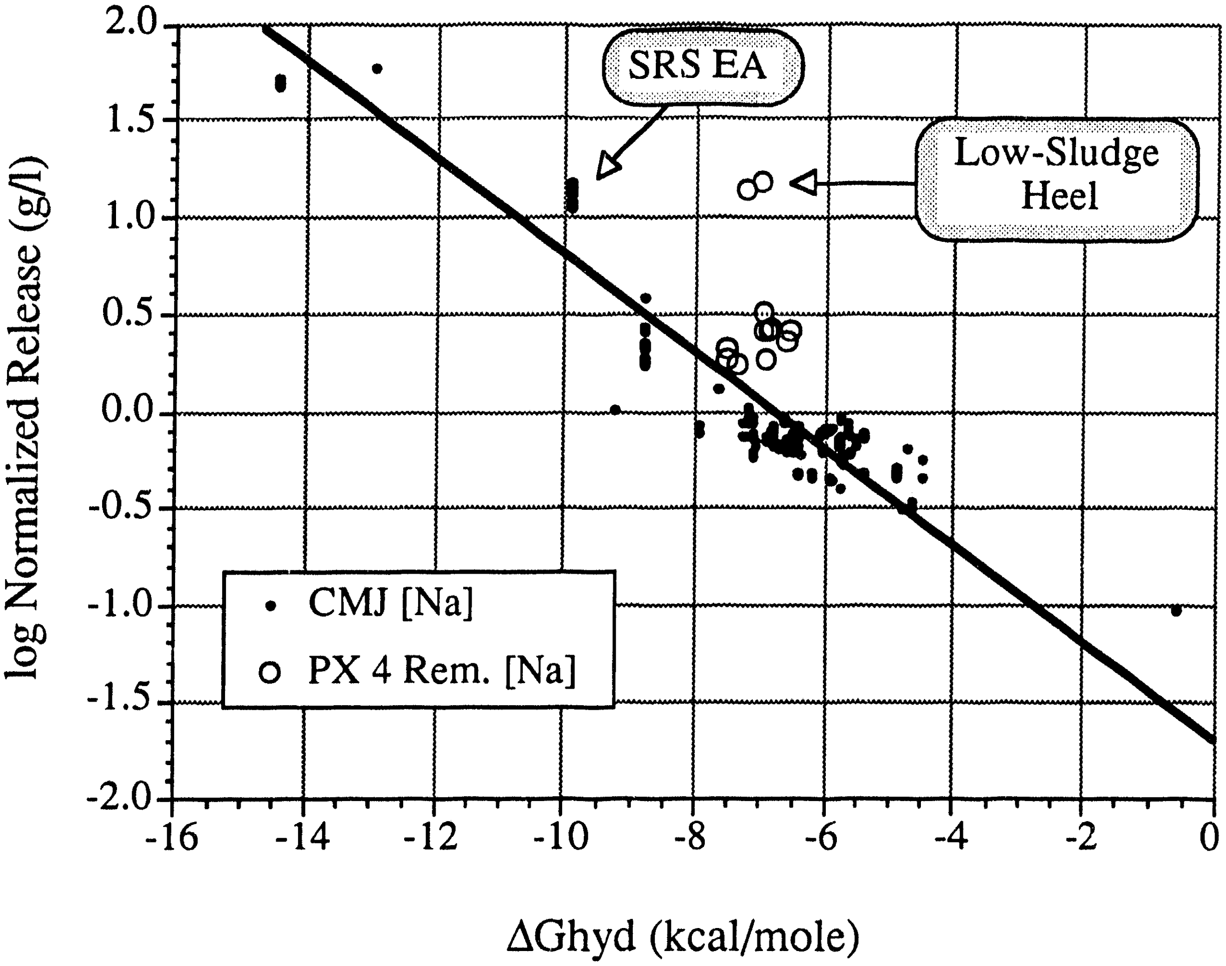

Figure 3. Relationship Between Purex 4 Remediation Glass Durability and Hydration Thermodynamics.

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Appendix 1

This appendix contains the PCT leachate concentrations of Na and B for the Purex 4 Remediation campaign. Triplicate values are reported for both Na and B, as well as mean and standard deviation. All values reported are in ppm. Cans 1X and 2X correspond to the positions -1 and 0, respectively, in Figures 1 and 2.

Element	**Can 1X**	**Can 2X**	**Can #1**	**Can #2**	**Can #3**
Na (ppm)	1280	1275	271	191	137
	1309	1248	303	176	149
	1539	1282	298	169	173
Mean	**1376**	**1268**	**291**	**179**	**153**
St. Dev.	142	18	17	11	18
B (ppm)	450	441	91	66.2	48.2
	458	427	102	60.6	53.1
	538	440	100	58.3	62.1
Mean	**482**	**436**	**98**	**61.7**	**54.5**
St. Dev.	48	7.5	6.2	4.1	7.1

Element	**Can #4**	**Can #5**	**Can #6**	**Can #7**	**Can #8**
Na (ppm)	133	186	165	184	218
	138	183	234	171	163
	141	191	160	180	181
Mean	**137**	**187**	**186**	**178**	**187**
St. Dev.	4.0	3.9	41.5	6.6	28.2
B (ppm)	47.4	79.1	62.7	71.8	88.5
	49.2	78.0	92.2	66.3	64.3
	50.3	81.5	60.3	70.1	71.7
Mean	**49.0**	**79.5**	**71.8**	**69.4**	**74.8**
St. Dev.	1.5	1.8	17.8	2.8	12.4

Appendix 1, continued

This appendix contains the PCT leachate concentrations of Na and B for the Purex 4 Remediation campaign. Triplicate values are reported for both Na and B, as well as mean and standard deviation. All values reported are in ppm. Glasses denoted EA and ARM-1 are control standards run to benchmark the PCT data set.

Element	**Can #9**	**Can #10**	Standard **ARM-1**	Standard **EA**
Na (ppm)	125	196	33.7	1811
	123	137	34.9	1824
	131	141	35.6	1828
Mean	**126**	**158**	**34.7**	**1822**
St. Dev.	4.0	33.1	0.9	8.7
B (ppm)	53.2	77.6	16.0	641
	52.5	52.5	16.7	646
	53.8	54.2	17.2	645
Mean	**53.2**	**61.4**	**16.6**	**644**
St. Dev.	0.7	14.0	0.6	2.9

Appendix 2

Analyzed compositions of the Purex 4 Remediation glasses. Glasses are identified by the can designation and SRTC Analytic Development Services (ADS) sample number. Glass samples 1X and 2X are from glass cans produced immediately prior to the Purex 4 Remediation campaign. Cans 1X and 2X correspond to the positions -1 and 0, respectively, in Figure 1. The Compositions are reported in normalized weight percent oxide. ΔG_{hyd} and $\Delta G_{hyd}(pH)$ values are reported in the units kcal/mole.

	Can 1X ADS 4268	Can 2X ADS 4267	Can #1 ADS 4252	Can #2 ADS 4254	Can #3 ADS 4256
Al_2O_3	2.42	2.59	3.29	3.29	3.20
CaO	0.84	0.89	1.08	1.20	1.26
Fe_2O_3	6.10	6.63	8.64	10.58	11.66
FeO	0.16	0.18	0.23	0.29	0.31
MgO	0.78	0.79	0.93	1.18	1.34
MnO	1.21	1.30	1.64	2.00	2.19
Na_2O	12.33	12.62	11.91	11.90	11.42
Li_2O	5.61	5.68	5.24	5.37	5.26
NiO	0.58	0.68	0.99	1.15	1.21
SiO_2	60.15	58.70	55.33	51.39	49.90
Cr_2O_3	0.12	0.14	0.24	0.24	0.23
B_2O_3	8.00	8.06	8.27	8.67	8.97
UO_2	0.00	0.00	0.00	0.00	0.00
ThO_2	0.00	0.00	0.00	0.00	0.00
SrO	0.02	0.03	0.03	0.03	0.02
ZrO_2	0.90	0.89	0.84	0.84	0.81
TiO_2	0.08	0.08	0.13	0.17	0.21
K_2O	0.22	0.24	0.54	0.94	1.18
Cs_2O	0.00	0.00	0.00	0.00	0.00
Sb_2O_3	0.00	0.00	0.00	0.00	0.00
P_2O_5	0.00	0.00	0.04	0.04	0.05
Nd_2O_3	0.00	0.00	0.00	0.00	0.00
La_2O_3	0.02	0.02	0.04	0.03	0.03
Y_2O_3	0.00	0.00	0.00	0.00	0.00
BaO	0.04	0.05	0.05	0.06	0.07
PbO	0.00	0.00	0.03	0.05	0.06
CeO_2	0.00	0.00	0.00	0.00	0.00
MoO_3	0.00	0.00	0.00	0.00	0.00
ZnO	0.36	0.37	0.34	0.33	0.31
CuO	0.06	0.06	0.16	0.25	0.31
ΔG_{hyd}	-6.96	-7.21	-6.95	-7.53	-7.53
Leachate pH	10.44	10.54	10.65	10.28	10.29
$\Delta G_{hyd}(pH)$	-9.51	-10.07	-10.01	-9.72	-9.74

Appendix 2, continued

Analyzed compositions of the Purex 4 Remediation glasses. Glasses are identified by the can designation and SRTC Analytic Development Services (ADS) sample number. The compositions are reported in normalized weight percent oxide. ΔG_{hyd} and $\Delta G_{hyd}(pH)$ values are reported in the units kcal/mole.

	Can #4 ADS 4258	Can #5 ADS 4263	Can #6 ADS 4242	Can #7 ADS 4244	Can #8 ADS 4246
Al_2O_3	3.04	2.62	2.72	2.66	2.62
CaO	1.29	1.20	1.28	1.26	1.28
Fe_2O_3	12.13	11.69	12.33	12.64	12.82
FeO	0.33	0.32	0.33	0.34	0.35
MgO	1.41	1.40	1.48	1.51	1.55
MnO	2.27	2.20	2.32	2.40	2.41
Na_2O	10.94	9.90	9.88	9.63	9.47
Li_2O	5.10	4.68	4.68	4.64	4.61
NiO	1.23	1.15	1.20	1.23	1.19
SiO_2	50.13	53.64	50.89	50.94	50.96
Cr_2O_3	0.21	0.19	0.16	0.15	0.14
B_2O_3	8.66	7.55	8.98	8.78	8.70
UO_2	0.00	0.00	0.00	0.00	0.00
ThO_2	0.00	0.00	0.00	0.00	0.00
SrO	0.02	0.02	0.01	0.00	0.01
ZrO_2	0.78	0.71	0.72	0.70	0.69
TiO_2	0.22	0.22	0.23	0.24	0.25
K_2O	1.41	1.67	1.91	2.02	2.17
Cs_2O	0.00	0.00	0.00	0.00	0.00
Sb_2O_3	0.00	0.00	0.00	0.00	0.00
P_2O_5	0.05	0.05	0.06	0.06	0.04
Nd_2O_3	0.00	0.00	0.00	0.00	0.00
La_2O_3	0.01	0.01	0.01	0.00	0.00
Y_2O_3	0.00	0.00	0.00	0.00	0.00
BaO	0.07	0.07	0.07	0.07	0.07
PbO	0.07	0.08	0.07	0.08	0.06
CeO_2	0.00	0.00	0.00	0.00	0.00
MoO_3	0.00	0.00	0.00	0.00	0.00
ZnO	0.31	0.29	0.28	0.25	0.21
CuO	0.35	0.36	0.38	0.40	0.41
ΔG_{hyd}	-7.33	-6.51	-6.92	-6.83	-6.81
Leachate pH	10.18	10.26	10.34	10.30	-9.20
$\Delta G_{hyd}(pH)$	-9.31	-8.66	-9.24	-9.06	10.37

Appendix 2, continued

Analyzed compositions of the Purex 4 Remediation glasses. Glasses are identified by the can designation and SRTC Analytic Development Services (ADS) sample number. The compositions are reported in normalized weight percent oxide. ΔG_{hyd} and ΔG_{hyd}(pH) values are reported in the units kcal/mole.

	Can #9 ADS 4248	Can #10 ADS 4265
Al_2O_3	2.58	2.53
CaO	1.31	1.31
Fe_2O_3	13.16	13.24
FeO	0.36	0.36
MgO	1.58	1.57
MnO	2.45	2.36
Na_2O	9.48	9.44
Li_2O	4.57	4.49
NiO	1.24	1.20
SiO_2	50.33	51.86
Cr_2O_3	0.13	0.14
B_2O_3	8.80	7.48
UO_2	0.00	0.00
ThO_2	0.00	0.00
SrO	0.01	0.01
ZrO_2	0.69	0.69
TiO_2	0.25	0.26
K_2O	2.26	2.10
Cs_2O	0.00	0.00
Sb_2O_3	0.00	0.00
P_2O_5	0.00	0.07
Nd_2O_3	0.00	0.00
La_2O_3	0.00	0.00
Y_2O_3	0.00	0.00
BaO	0.07	0.08
PbO	0.05	0.09
CeO_2	0.00	0.00
MoO_3	0.00	0.00
ZnO	0.25	0.31
CuO	0.42	0.44
ΔG_{hyd}	-6.90	-6.55
Leachate pH	10.09	10.24
ΔG_{hyd}(pH)	-8.70	-8.65

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