

LEACHING OF BOROSILICATE GLASS USING DRAFT ASTM PROCEDURE FOR HIGH-LEVEL WASTE

Prepared for

**Nuclear Regulatory Commission
Contract NRC-02-88-005**

Prepared by

**Center for Nuclear Waste Regulatory Analyses
San Antonio, Texas**

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ABSTRACT

The main objective of the experimental investigation reported was to calibrate the aqueous leaching protocol for vitrified wasteforms with other laboratories involved in developing and testing of wasteforms for high-level radioactive wastes. The results of three experimental runs of aqueous leaching tests conducted on four types of borosilicate glasses, namely SRL 202-P, SRL 202-G, ARM-1, and SRM-623, are presented. The tests were conducted per the draft ASTM "Product Consistency Test (PCT)" procedure for high-level vitrified wasteforms. This test uses powdered glass with particle size between 100 and 200 ASTM mesh. Only nonradioactive glasses were used in the investigation reported here. The principal test parameters and environmental conditions are deionized water leachant at 90°C, closed-system static water environment, and sample mass (g) to leachate volume (mL) ratio of 0.1 g·mL⁻¹. The nominal test duration is 7 days. The leachates were analyzed for concentrations of Al, B, Li, Na, K, and Si, upon completion of the test, using inductively coupled plasma (ICP) spectroscopic technique. The final pH values for the leachate were also measured. The CNWRA test data show that the leachate concentrations for the high release elements (Li, B, Na, K) and the matrix element (Si) as well as the final pH are generally within two standard deviations of the values reported for the round robin tests conducted earlier in which participants were mostly from the DOE laboratories (CNWRA was not a participant). The precision of the CNWRA-generated data was sufficient to discriminate between two similar borosilicate waste glasses (same frit based) but with slightly different chemical durability. The durability rank ordering of the four glasses tested, based on CNWRA test data, matches that based on the round robin data. It is concluded that CNWRA laboratory protocol for conducting PCT is in calibration with the other laboratories that participated in the round robin tests and that CNWRA can provide independent experimental confirmation of DOE-generated data on borosilicate glass wasteforms being developed for geological disposal of HLW.

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1 INTRODUCTION

The majority of the high-level radioactive wastes (HLW) in the United States arise from reprocessing of the irradiated fuel from the defense reactors. However, a small volume has been accumulated from the limited reprocessing of commercial power reactors spent fuels. Currently, these wastes are stored as liquid in large underground tanks with individual tank capacities of several million liters. Both defense and commercial HLW are planned to be converted into a solid form by incorporating them into a borosilicate glass matrix. The glass (vitrified) wasteform is planned to be solidified in a Type 304L stainless steel canister and subsequently provided with an outer overpack container to form a waste package. Eventually, these waste packages are to be permanently placed in a deep geologic formation with suitable characteristics to isolate the radionuclides from the biosphere for a long period of time.

The U.S. HLW vitrification program is on a very large scale, involving over 15,000 packages for the first repository. These HLW packages are likely to take two decades or more to fabricate. To keep the products reasonably constant over such a long period of time requires control of the chemical composition and the manufacturing process. The consistency of the product (borosilicate glass wasteform) is to be demonstrated via a short-term laboratory test. The U.S. Department of Energy (DOE) intends to do this by conducting aqueous leaching tests on samples of the product. The test chosen by the DOE is called the "Product Consistency Test (PCT)." This test has been developed by the Savannah River Laboratory, Aiken, South Carolina, and is currently undergoing standardization in the Sub-Committee C26.13 on Nuclear Repository Materials and Testing of the Committee C26 on Nuclear Fuel Cycle, within the American Society for Testing and Materials (ASTM) organization. An ASTM Standard PCT Procedure for Nuclear Waste Glasses is expected to be issued in the near future.

The DOE is in the process of issuing a revised version of an earlier document titled "Waste Acceptance Preliminary Specifications (WAPS) for Vitrified High-Level Waste Forms," which will provide the numerical values for acceptable releases from HLW glasses in PCT (DOE, 1991). For the fabricated wasteform to be acceptable from the point of "consistency" of the product, the concentrations of lithium, sodium, and boron in the leachate, after normalizing for concentrations in the glass, are required to be at least two standard deviations below the mean PCT results of the DOE's Environmental Assessment (EA) glass. The EA glass is a DOE benchmark. The elemental release numbers for the EA glass in a PCT had not officially been announced by the DOE at the time of this report; however, they are expected to be $500 \text{ mg} \cdot \text{L}^{-1}$ or higher for the three alkalis required to be measured and reported.

The development of the PCT which utilized both an intralaboratory and an interlaboratory round robin with nonradioactive simulated waste glasses are reported in the literature (Jantzen and Bibler, 1987; Piepel et al., 1989). The emphasis during the test development was on generating a methodology that could be routinely performed on both radioactive and nonradioactive (simulated waste) glasses and yield results capable of evaluating comparable durabilities. The main purpose of the referenced round robins was to determine the precision of the PCT when performed by a single investigator and when performed by different investigators in different laboratories. Results of the earlier round robins indicated that for a single investigator a relative precision of 3 to 5 percent could be expected in triplicate tests. For different investigators and different laboratories, the relative precision decreased to 10 to 15 percent (Jantzen and Bibler, 1987; Piepel et al., 1989).

The main purpose of the work reported here was to calibrate the CNWRA test procedure for conducting leaching tests on glasses using PCT with other laboratories. Validation of the testing protocols, via comparison of the results with the round robin results, would also assure that the CNWRA has capability for independent verification of DOE-produced leaching test data on the vitrified wasteforms being developed for geological disposal. A summary of the results of the investigation are provided.

2 SCOPE OF THE INVESTIGATION

The scope of the investigation reported here was to conduct three runs of PCT according to the draft ASTM procedure using a test matrix with four types of DOE-provided borosilicate glass samples. Each run was to consist of triplicate samples of each glass including triplicate blanks (no glass) of deionized water leachate. The conduct of the test at the CNWRA was to include all necessary steps after the receipt of the solid glass samples from the DOE laboratory. [These steps include glass sample preparation (glass crushing, sieving, washing, and weighing), leachate preparation (ASTM Type I deionized water), cleaning of leaching vessels (hydrochloric/hydrofluoric acid grease stripping of new leaching vessels, dilute nitric acid cleaning), leaching vessel assembly (including verification of mass loss of leachate from new leaching vessels within the ASTM specifications), calibration of low-temperature forced-air oven with calibrated thermometers/thermocouple, exposure of the test assembly to controlled temperature for a specified period of time, leaching vessel disassembling, extraction and filtration of the leachate upon completion of the test, pH measurement of the leachate, acidification of the leachates to avoid precipitation of certain elements upon cooling, preparation of coded leachate specimens (including blind blanks) for elemental analyses by inductively coupled plasma (ICP) spectroscopic technique, and data reduction and analyses.] The release rates of Al, Fe, B, Li, Na, K, and Si were to be reported, and comparison of elemental releases of Li, B, and Na (which are required to be reported by DOE per WAPS) were to be made with the earlier conducted PCT round robin. (The CNWRA did not participate in that round robin). The validation of the calibration of the CNWRA protocol for conducting PCT was to be based on the CNWRA results falling within a range of two standard deviations of the means reported for the round robin, and by the ability of CNWRA results to discriminate between two similar borosilicate glasses (based on the same frit), namely, SRL 202-G and SRL 202-P, which have a small difference in their chemical durability (SRL 202-P glass being less durable than SRL 202-G glass).

3 MATERIALS, LEACHING TEST ASSEMBLY, AND TEST PROTOCOL

3.1 TEST MATERIALS AND COMPOSITION

Four types of borosilicate glasses containing simulated high-level wastes were included in the investigation. These are SRL 202-G, SRL 202-P, ARM-1, and SRM-623. The first two are the Savannah River Laboratory (SRL) produced glasses specially formulated to check the sensitivity of the PCT, while the latter two are reference borosilicate glasses produced by the Pacific Northwest Laboratory (PNL) and the National Institute for Standards and Technology (NIST), respectively. The compositions of the four test glasses are shown in Table 3-1 (Piepel et al., 1989). The presence of potassium in the SRL glasses is used to simulate the precipitate hydrolysis product that will result from the in-tank precipitation of Cs-137 (Bibler and Bates, 1989). The SRL 202-P glass was formulated with a larger amount of potassium to represent off-normal composition. The analyses of the composition were conducted independently by SRL and PNL for the SRL 202-G and SRL 202-P glasses. The ARM-1 and SRM-623 glasses were analyzed by PNL only. The certified/nominal compositions for these two glasses are also given in Table 3-1. As shown in the referenced table, the difference between the two independent analyses or the certified/nominal value and the analyses is less than 10 percent for major components of the glass (those > 1 wt% of the total composition). For the minor components, such as NiO, CuO, SrO, etc., the differences in the analyses are much higher, ranging up to 50 percent for CuO. The composition of the glass samples sent to CNWRA were not analyzed and are presumed to have generally the same compositions as the earlier round robin glasses as shown in Table 3-1 (Piepel et al., 1989). The test samples were supplied to the CNWRA by the Savannah River Laboratory in the quantity of approximately 100 g each. The glass types SRL 202-G and 202-P were in the form of four to 10 pieces each, while ARM-1 and SRM-623 glasses were in the form of smaller pieces (several dozen to hundreds of pieces) in various sizes ranging from fines to 0.5 cm or more in diameter. Only larger size pieces were used to prepare the samples for the CNWRA experiments.

3.2 SPECIMEN PREPARATION

The samples were prepared by mechanically crushing blocks of glass in a coffee-mill type grinder with a tungsten carbide blade (to avoid contamination of the glass from a standard steel blade typically supplied with such grinders). The crushing procedure involved crushing ~5 to 10 g pieces of glass in a tungsten carbide disk mill for ~5 seconds. The crushed glass was then placed in a sieving equipment with a stack of sieves in the order (from top to bottom) of 70 mesh, 100 mesh, 200 mesh, 270 mesh, and 400 mesh. The sieves were vibrated and tapped with an electric device to fractionate the crushed glass. After about 10 minutes, the sieve assembly was dismantled and the crushed glass in the -100 to +200 mesh fraction was transferred to a clean plastic container. This fraction of the crushed glass was then washed with deionized water followed by alcohol using an ultrasonic cleaner. The washed glass was dried overnight in a 90°C forced-air oven. Washed and dried glass was then transferred to a labeled bottle identifying the glass type, ready for testing. Additional details of the test equipment are available in the draft ASTM PCT procedure (Jantzen et al., 1991).

Table 3-1. Composition Analyses of the Glasses Tested, wt% (Adapted from Piepel et al., 1989)

Compound	SRL 202-G			SRL 202-P			ARM-1			SRM-623		
	SRL Anal.	PNL Mean	Diff. %	SRL Anal.	PNL Mean	Diff. %	Cert. Val.	PNL Mean	Diff. %	NIST Nom.	PNL Mean	Diff. %
Al ₂ O ₃	4.40	4.59	+4.14	4.14	4.27	+3.04	5.59	5.78	+3.29	6.3	6.14	-2.61
B ₂ O ₃	5.82	6.00	+3.00	8.25	8.49	+2.83	11.30	11.80	+4.24	10.7	10.10	-5.90
BaO	0.15	0.14	-7.14	0.20	0.18	-11.11	0.658	0.65	-1.23	2.2	2.00	-10.00
CaO	1.32	1.31	-0.76	1.32	1.30	-1.54	2.24	2.32	+3.45	0.7	0.69	-1.45
CeO ₂	—	—	—	—	—	—	1.51	1.42	-6.33	—	—	—
Cr ₂ O ₃	0.15	0.10	-50.00	0.15	0.10	-50.00	—	—	—	—	—	—
Cs ₂ O	n.d.	0.03	—	n.d.	0.13	—	1.17	1.08	-8.33	—	0.03	—
CuO	0.40	0.37	-8.11	0.67	0.64	-4.64	—	—	—	—	—	—
Dy ₂ O ₃	—	—	—	—	—	—	—	0.02	—	—	—	—
Eu ₂ O ₃	—	—	—	—	—	—	—	0.02	—	—	—	—
Fe ₂ O ₃	12.53	12.03	-4.16	11.51	10.63	-8.28	—	0.05	—	—	0.09	—
K ₂ O	2.83	3.24	+12.65	4.82	6.06	+20.46	—	—	—	0.6	1.00	+40.00
La ₂ O ₃	—	—	—	—	—	—	—	0.02	—	—	—	—
Li ₂ O	3.67	3.80	+3.42	3.29	3.41	+3.52	5.08	4.82	-5.39	—	—	—
MgO	3.30	3.13	-5.43	3.07	2.84	-8.10	—	—	—	—	—	—
MnO ₂	—	0.02	—	—	0.01	—	—	0.01	—	—	—	—
MoO ₃	—	—	—	—	—	—	1.66	1.91	+13.09	—	—	—
Na ₂ O	6.92	8.28	+16.43	7.52	9.13	+17.63	9.66	9.73	+0.72	6.4	6.46	+0.93
Nd ₂ O ₃	—	—	—	—	—	—	5.96	5.52	-7.97	—	—	—
NiO	0.74	0.64	-15.63	0.78	0.66	-18.18	—	—	—	—	—	—
P ₂ O ₅	—	—	—	—	—	—	0.65	—	—	—	—	—
RhO ₂	—	—	—	—	—	—	—	—	—	—	—	—
RuO ₂	—	—	—	—	—	—	—	—	—	—	—	—
SiO ₂	56.63	53.97	-4.93	52.91	50.83	-4.09	46.50	45.60	-1.97	73.0	71.40	-2.24
SrO	—	0.01	—	—	0.01	—	0.453	0.47	+3.62	—	0.03	—
TiO ₂	0.67	0.65	-3.08	1.22	1.16	-5.17	3.21	3.32	+3.31	—	0.02	—
Y ₂ O ₃	—	—	—	—	—	—	—	—	—	—	—	—
ZnO	—	—	—	—	—	—	1.46	1.47	0	—	—	—
ZrO ₂	—	0.03	—	—	0.03	—	1.80	1.87	+3.74	—	0.05	—

3.3 LEACHING VESSEL ASSEMBLY

Leaching vessels of 45 mL capacity fabricated from Type 304L stainless steel were used for the experiment. The leaching vessels were cleaned using the draft ASTM PCT procedure (Jantzen et al., 1991). Three glass specimen sizes 1.5g, 2.5g, and 4.0 g were used in the test. Test Run #1 used only 1.5 g specimens, while Test Run #2 and Run #3 used one specimen of 1.5 g, one of 2.5 g, and one of 4.0 g, representing triplicate specimens for each type of glass. The amount of deionized water leachate to be added was calculated as 10 mL for each gram of the glass specimen used. In addition, three blanks (deionized water with no glass) were used in each test run. The leaching vessel assemblies were prepared by closing the cylindrical vessel with a Type 304L stainless steel lid. The lid was equipped with a Teflon washer and was tightly held to the leaching vessel with an independent threaded nut subassembly. The assembled leaching vessels were weighed prior to inserting them in the oven.

3.4 TEST PROCEDURE

The assembled leaching vessels were hung vertically in a preheated forced-air oven maintained at 90°C. After 1 day, the leaching vessel assemblies were removed from the oven, cooled to room temperature, and weighed to check for mass loss due to any leaks according to the draft procedure. The reweighed assemblies were reinserted in the oven for an additional 6 days exposure. They were then removed from the oven, cooled to room temperature, and weighed again for mass according to the test procedure. The assemblies were then disassembled one at a time to extract the leachate.

3.5 LEACHATE EXTRACTION

The leachate was extracted and transferred to a clean plastic container using a syringe with a stainless steel hypodermic needle. A small quantity of the leachate was removed for measuring pH of the solution. Thereafter, the leachate was filtered through a 0.45-micron cellulose acetate filter to remove any glass particles. The filtered leachate was acidified using 1 percent HNO₃ solution in the ratio of one part leachate to 20 parts dilute nitric acid. The required number of splits of the leachates were prepared and labeled with the appropriate identification for the glass type or blank, and the run number, prior to submitting them for analyses. The analyses of the leachate were conducted for a number of elements using the ICP technique. However, this report only provides the releases of Al, B, Na, K, Li, Fe, and Si. The discussion is mainly on the concentrations of B, Li, Na, K, and Si, as these were the only elements on which the earlier round robin investigation was based.

3.6 DIFFERENCES BETWEEN ROUND ROBIN AND CNWRA TEST PROTOCOL

There are three major differences in the test protocols of the earlier conducted round robin and the CNWRA-conducted leaching tests. These are: (i) the round robin participants did not wash the crushed glass to remove the fines prior to conducting the leaching test [the round robin was based on an earlier version of the PCT procedure that did not require washing of the crushed glass specimens (Piepel et al., 1989)]; (ii) the leaching vessels used by the round robin participants were 50 mL capacity and were fabricated from Teflon, while the CNWRA tests used 45 mL capacity vessels fabricated from Type 304L stainless steel, with a Teflon washer; and (iii) the round robin participants used only 4.0 g size crushed glass samples in all tests, while the CNWRA experimented with 1.5 g, 2.5 g, and 4.0 g specimen size. However, as mentioned earlier, the ratio of solution-volume to solid-mass was the same in all these tests.

4 TEST DATA AND ANALYSES

The test data from the earlier round robin and the CNWRA PCT leaching experiments are provided in Table 4-1. This table shows the mean, standard deviation (SD), and relative standard deviation (%RSD) for the four borosilicate glasses investigated. All plotted data are rounded off to the nearest mg/L concentration. The round robin data are based on input from all except one participating laboratory (Piepel et al., 1989). The data for the CNWRA laboratory is reported separately for Run #1, and averaged for Runs #2 and #3. The reason for this is that the two subsets of CNWRA data clearly fall into two distinct distributions. The mean values and standard deviations for Run #1 were computed from independent analyses of two splits of each of the triplicate samples for each glass (i.e., they represent six individual elemental analyses). For Runs #2 and #3, the data are averaged for the triplicate samples from each of these runs for each type of glass (i.e., the mean values and standard deviations represent six individual elemental analyses). The smaller size of the specimens in Run #1 does not appear to be the reason for the difference between the leachate concentrations between Run #1 and Runs #2 and #3. [As stated earlier, Run #1 used 1.5 g size specimens, while Runs #2 and #3 used 1.5 g, 2.5 g, and 4 g size specimens. The releases from 1.5 g, 2.5 g, and 4.0 g samples, from Runs #2 and #3, did not indicate any specimen size effect]. Although no definitive explanation for the bimodal distribution for the CNWRA data is available, unfamiliarity with the application of a new procedure for the preparation of specimens for Run #1, particularly crushing, sieving, and washing steps, could possibly have contributed to the lower releases in Run #1 as compared to Runs #2 and #3. (Fresh samples were prepared for each run). However, the possibility of a systematic error in the analyses of the leachates from Run #1 also exists. This error could be investigated further by using archive leachates from Run #1. It is worth noting that the data for Runs #2 and #3 are very consistent as shown by the smaller standard deviations as compared to those of the round robin tests.

Table 4-1. Leachate Elemental Analyses and Final pH

Glass Type	Analyte	Mean ^(a)			Standard Deviation ^(b)			%RSD ^(c)		
		Round Robin ^(d)	CNWRA Run #1 ^(e)	CNWRA Runs #2 and #3 ^(f)	Round Robin	CNWRA Run #1	CNWRA Runs #2 and #3	Round Robin	CNWRA Run #1	CNWRA Runs #2 and #3
SRL 202-P	Al	3.508	4.219	5.632	0.288	0.203	0.834	8.22	4.81	14.80
	B	25.28	18.57	24.55	1.269	0.643	0.635	5.02	3.46	2.58
	Fe	4.069	3.669	9.780	1.043	0.640	3.851	25.64	17.44	39.37
	K	32.30	23.50	29.68	2.892	0.312	0.458	8.95	1.32	1.54
	Li	15.87	10.32	13.63	0.817	0.127	0.385	5.15	1.23	2.82
	Na	69.64	45.42	61.88	3.901	0.648	1.542	5.60	1.42	2.49
	Si	109.6	94.01	113.2	3.761	5.000	4.087	3.43	5.32	3.60
	pH	10.63	9.847	10.49	0.408	0.535	0.072	3.84	5.43	0.68

SRL 202-G	Al	3.872	4.391	5.024	0.343	0.247	0.546	8.86	5.62	10.86
	B	14.44	11.57	13.84	0.724	0.263	0.262	5.01	2.27	1.89
	Fe	3.836	3.870	6.891	0.968	0.881	2.328	25.24	22.76	33.78
	K	11.53	9.84	11.21	2.185	0.292	0.674	18.94	2.96	6.00
	Li	15.22	10.37	12.46	0.734	0.089	0.267	4.82	0.85	2.14
	Na	49.86	37.79	43.41	2.493	0.905	0.858	5.00	2.39	1.97
	Si	112.3	100.1	115.2	4.175	1.220	2.391	3.72	1.21	0.20
	pH	10.42	10.25	10.31	0.415	0.022	0.067	3.98	0.21	0.64

ARM-1	Al	4.652	4.742	4.452	0.468	0.166	0.353	10.06	3.50	7.92
	B	27.48	29.46	26.17	3.335	1.347	3.023	12.13	4.57	11.54
	Fe ^(w)	0.117	0.124	0.293	0.313	0.078	0.195	267.5	62.90	66.55
	K ^(w)	0.549	0.356	0.671	0.696	0.119	0.207	126.8	33.42	30.84
	Li	21.73	20.47	17.63	1.540	0.681	1.486	7.09	3.32	8.42
	Na	55.64	53.56	48.08	5.082	1.911	4.113	9.13	3.56	8.55
	Si	80.16	82.03	73.77	6.031	1.850	3.466	7.52	2.25	4.69
	pH	10.56	10.41	10.38	0.373	0.112	0.080	3.53	1.07	0.77

Table 4-1. Leachate Elemental Analyses and Final pH (Cont'd)

Glass Type	Analyte	Mean ^(a)			Standard Deviation ^(b)			%RSD ^(c)		
		Round Robin ^(d)	CNWRA Run #1 ^(e)	CNWRA Runs #2 and #3 ^(f)	Round Robin	CNWRA Run #1	CNWRA Runs #2 and #3	Round Robin	CNWRA Run #1	CNWRA Runs #2 and #3
SRM-623	Al	3.343	—	3.041	0.228	—	0.142	6.83	—	4.67
	B	7.050	—	4.876	0.609	—	0.097	8.64	—	1.99
	Fe ^(g)	0.056	—	0.240	0.104	—	0.103	184.8	—	42.92
	K ^(g)	0.600	—	0.334	0.665	—	0.336	110.7	—	100.6
	Li ^(g)	0.054	—	0.179	0.082	—	0.031	150.3	—	17.32
	Na	12.73	—	8.075	0.961	—	0.251	7.55	—	3.11
	Si	46.09	—	39.95	4.465	—	1.022	9.69	—	2.56
	pH	8.692	—	8.689	0.280	—	0.080	3.23	—	0.92

- (a) Mean values of analyte concentrations are given in units of mg/L.
- (b) All standard deviations are in units of mg/L and quantify the uncertainty in a single value.
- (c) %RSD is obtained by dividing the corresponding standard deviation value by the mean and multiplying by 100.
- (d) Data from the round robin.
- (e) Data from CNWRA Run #1.
- (f) Data from CNWRA Runs #2 and #3 averaged.
- (g) These elements were not present in the glass; therefore, the means and standard deviations characterize detection-limit noise.

5 DISCUSSION

The elemental release data, from Table 4-1, for the highly soluble elements, namely, B, K, Li, and Na, and the matrix element Si are shown in Figures 5-1 through 5-5. The pH values are shown in Figure 5-6. These figures show the mean values for the concentration of specific elements for the round robin (with one, two, and three standard deviation error bars), and for the CNWRA experiments separately for Run #1, and averaged for Runs #2 and #3 (with one standard deviation error bar). Run #1 data represents a mean for the six data points per glass type obtained by analyzing the leachate from triplicate samples (two independent analyses of leachate from each leaching vessel), while the data from Runs #2 and #3 are based on six independent leachate analyses per glass type (triplicate samples of each glass type per run). An examination of the data reveals that elemental releases observed in the CNWRA tests are consistently lower than those reported for the round robin, but are generally within two standard deviations of the mean values for the round robin. Data from CNWRA Run #1 is generally lower than the averaged data from Runs #2 and #3.

5.1 INDIVIDUAL ELEMENTAL RELEASES

On individual element release basis, for boron, as shown in Figure 5-1, the CNWRA Runs #2 and #3 data are within one standard deviation for glass types SRL 202-P, 202-G, and ARM-1. For potassium, as shown in Figure 5-2, the results of CNWRA Runs #2 and #3 are within one standard deviation for glass types SRL 202-P and 202-G (other glasses investigated did not contain potassium). For lithium, as shown in Figure 5-3, the CNWRA Runs #2 and #3 releases for glasses SRL 202-P and 202-G, are within two standard deviations of the round robin data, and for the ARM-1 glass the data are slightly outside the two standard deviations of the round robin mean. However, the mean values of the CNWRA data are consistently lower than round robin data for these three glasses. (Glass SRM-623 is not shown in Figure 5-3 as it did not contain lithium). For sodium, as shown in Figure 5-4, the CNWRA Runs #2 and #3 data are within two standard deviations of the round robin mean for the glass types 202-P and ARM-1, and slightly outside this range for glass types SRL 202-G and SRM-623. For silicon, as shown in Figure 5-5, for all glasses, the CNWRA Runs #2 and #3 data are within two standard deviations of the round robin. For the glass types SRL 202-P and SRL 202-G, the mean CNWRA silicon releases are slightly higher than round robin, while for the other two glass types, ARM-1 and SRM-623, they are slightly lower. An examination of the data in Figure 5-6 indicates that the final leachate pH values for CNWRA Runs #2 and #3 are within one standard deviation of the round robin results, while the data for Run #1 are within two standard deviations of the round robin.

5.2 CUMULATIVE ELEMENTAL RELEASES

The cumulative releases for a group of elements are shown in Figure 5-7. (Glass type SRM-623 is not shown because it did not contain lithium). Group 1 shows cumulative releases for [B+Li+Na] for the glass types SRL 202-G, SRL 202-P, and ARM-1. Group 2 shows releases for the same three types of glasses for the [B+Li+Na+Si] combination, while Groups 3 and 4 show releases only for SRL 202-G and SRL 202-P glasses for the elemental combinations [B+K+Li+Na] and [B+K+Li+Na+Si], respectively. (Other glass types are not evaluated for these combinations of elements as they do not contain potassium). Based on the data shown in Figure 5-7, a rank ordering of the durability of the four glasses tested can be inferred as tabulated in Table 5-1. The results show that CNWRA rank ordering (using Runs #2 and #3 averaged data) agree exactly with that of the round robin, while based on CNWRA Run #1 data the rank ordering agrees with the round robin for the majority of the glasses with the main difference being the interchange of 202-P and ARM-1 glass rankings.

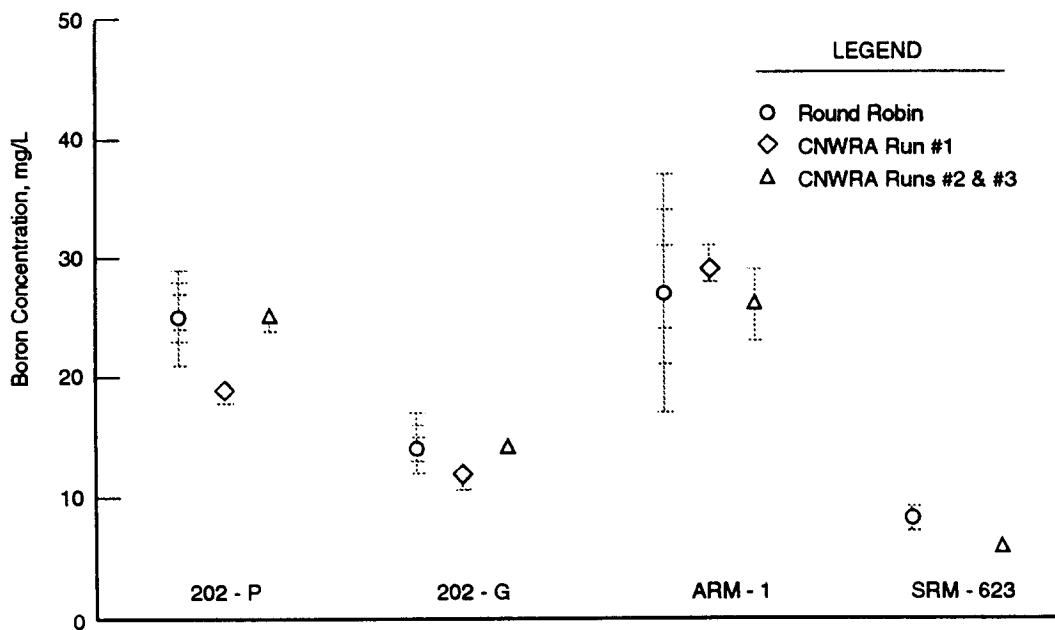


Figure 5-1. Release of Boron as a Function of Glass Type

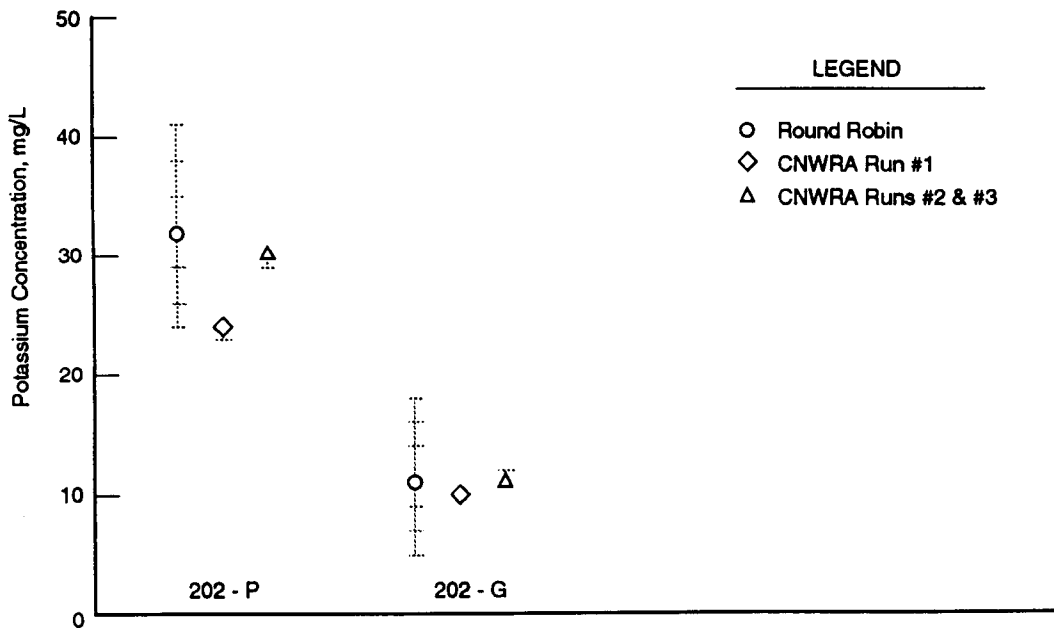


Figure 5-2. Release of Potassium as a Function of Glass Type

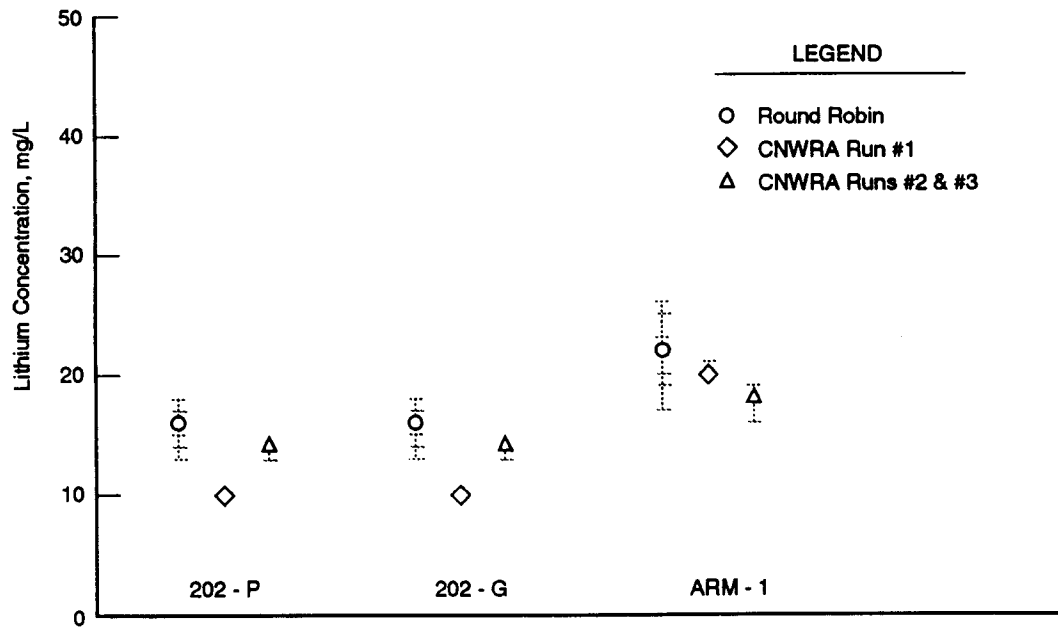


Figure 5-3. Release of Lithium as a Function of Glass Type

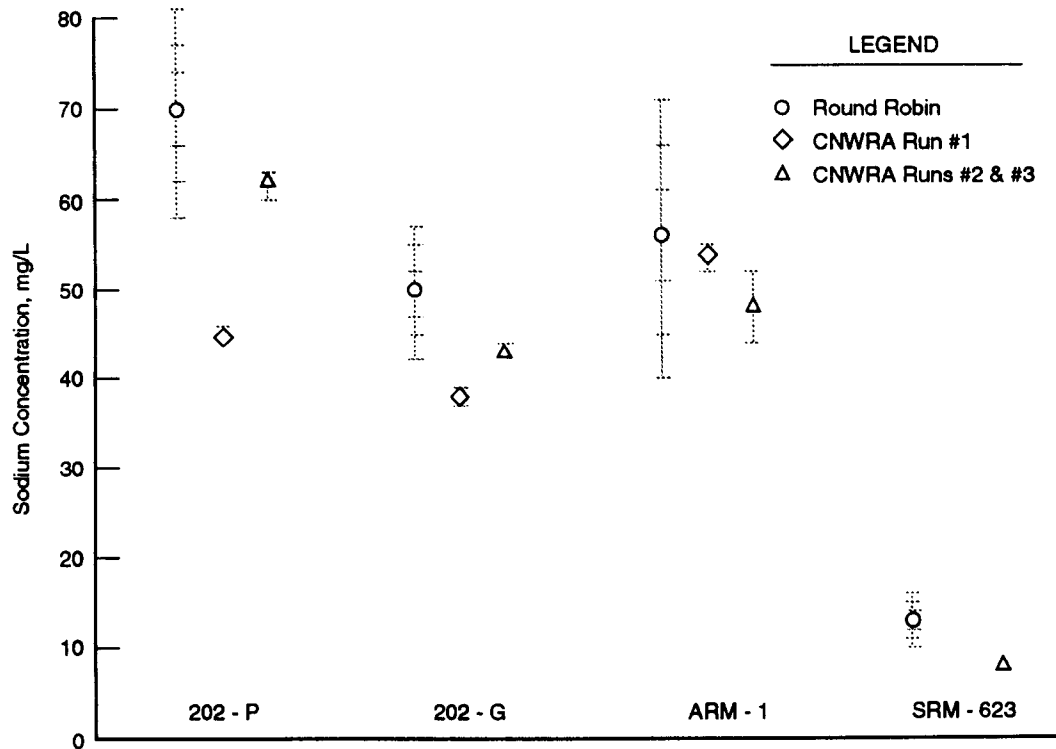


Figure 5-4. Release of Sodium as a Function of Glass Type

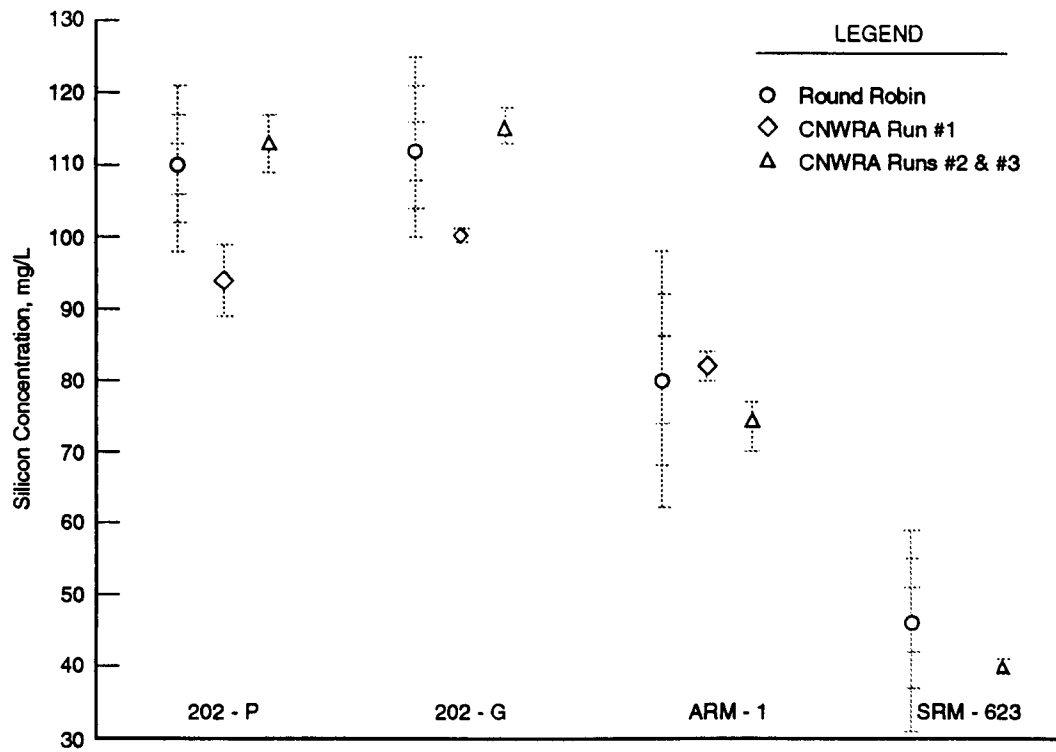


Figure 5-5. Release of Silicon as a Function of Glass Type

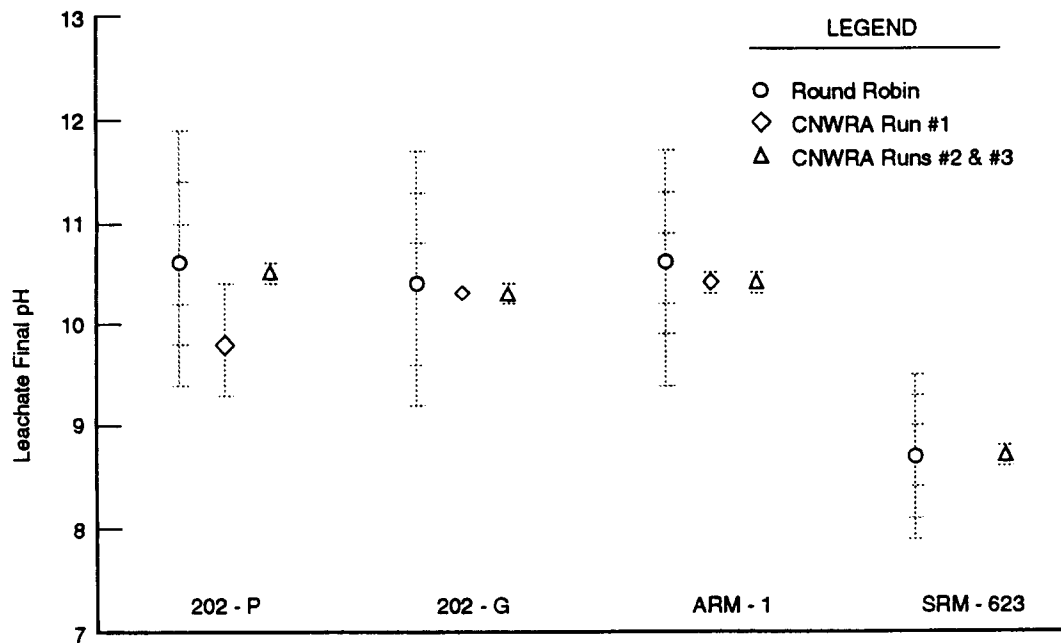


Figure 5-6. Final Leachate pH as a Function of Glass Type

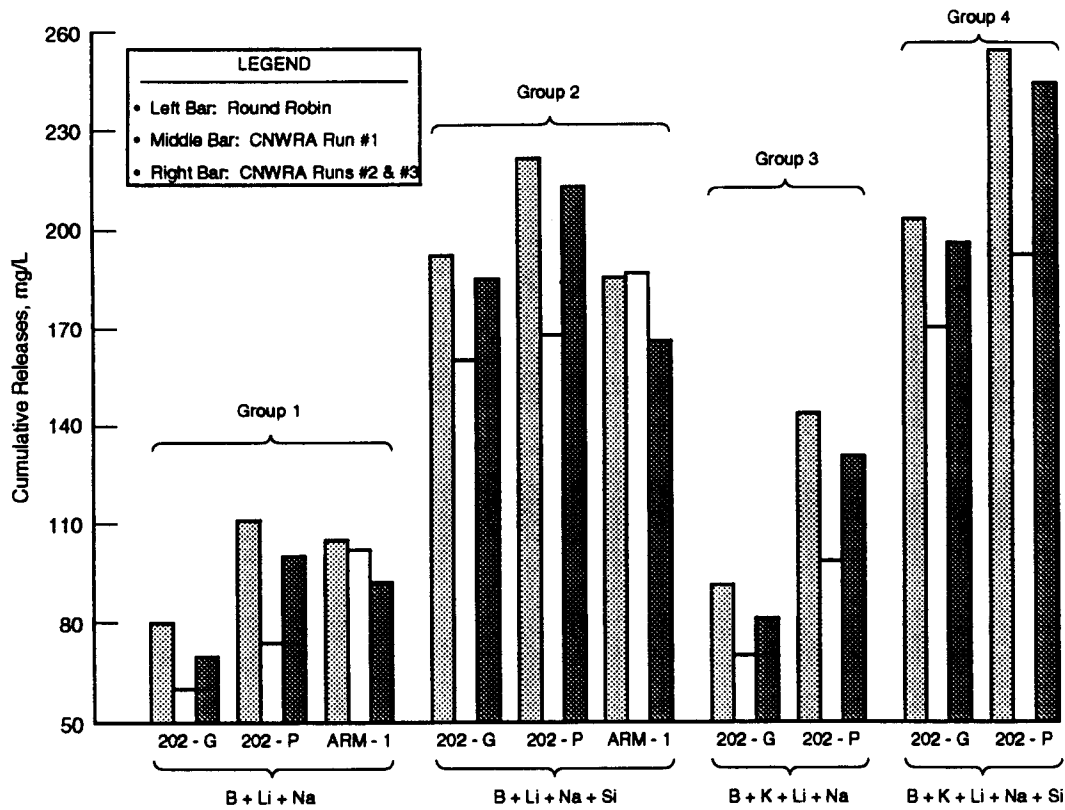


Figure 5-7. Cumulative Releases of Groups of Elements as a Function of Glass Type

Table 5-1. Ranking of Glasses Tested Based on Cumulative Releases for Groups of Elements

Glass Type	B + Li + Na			B + Li + Na + Si			B + K + Li + Na			B + K + Li + Na + Si		
	Round Robin	CNWRA Run #1	CNWRA Runs #2 and #3	Round Robin	CNWRA Run #1	CNWRA Runs #2 and #3	Round Robin	CNWRA Run #1	CNWRA Runs #2 and #3	Round Robin	CNWRA Run #1	CNWRA Runs #2 and #3
202-P	A	B	A	A	B	A	A	A	A	A	A	A
202-G	C	C	C	B	C	B	B	B	B	B	B	B
ARM-1	B	A	B	C	A	C	-	-	-	-	-	-
SRM-623*	D	-	D	D	-	D	-	-	-	-	-	-

* No lithium.
 # A → Least durable (most leachable)
 B → Second least durable
 C → Third least durable
 D → Most durable (least leachable)

5.3 COUPLED RELEASES FOR WAPS RELATED ELEMENTS

An attempt was made to explore if there was any systematic trend or relationship between the coupled releases of the three alkali elements that are required to be reported per WAPS for all production glasses, namely, lithium, sodium, and boron. Figure 5-8 shows releases for Li-Na-B and K-Na-B ternaries. For each ternary representation, the sum of releases (mg/L) are normalized to 100 mg/L. Since SRM-623 and ARM-1 did not contain lithium, their alkali element releases are shown on the binary Na-B axis. The plot shows values for both round robin and the CNWRA experiments (averaged data from Runs

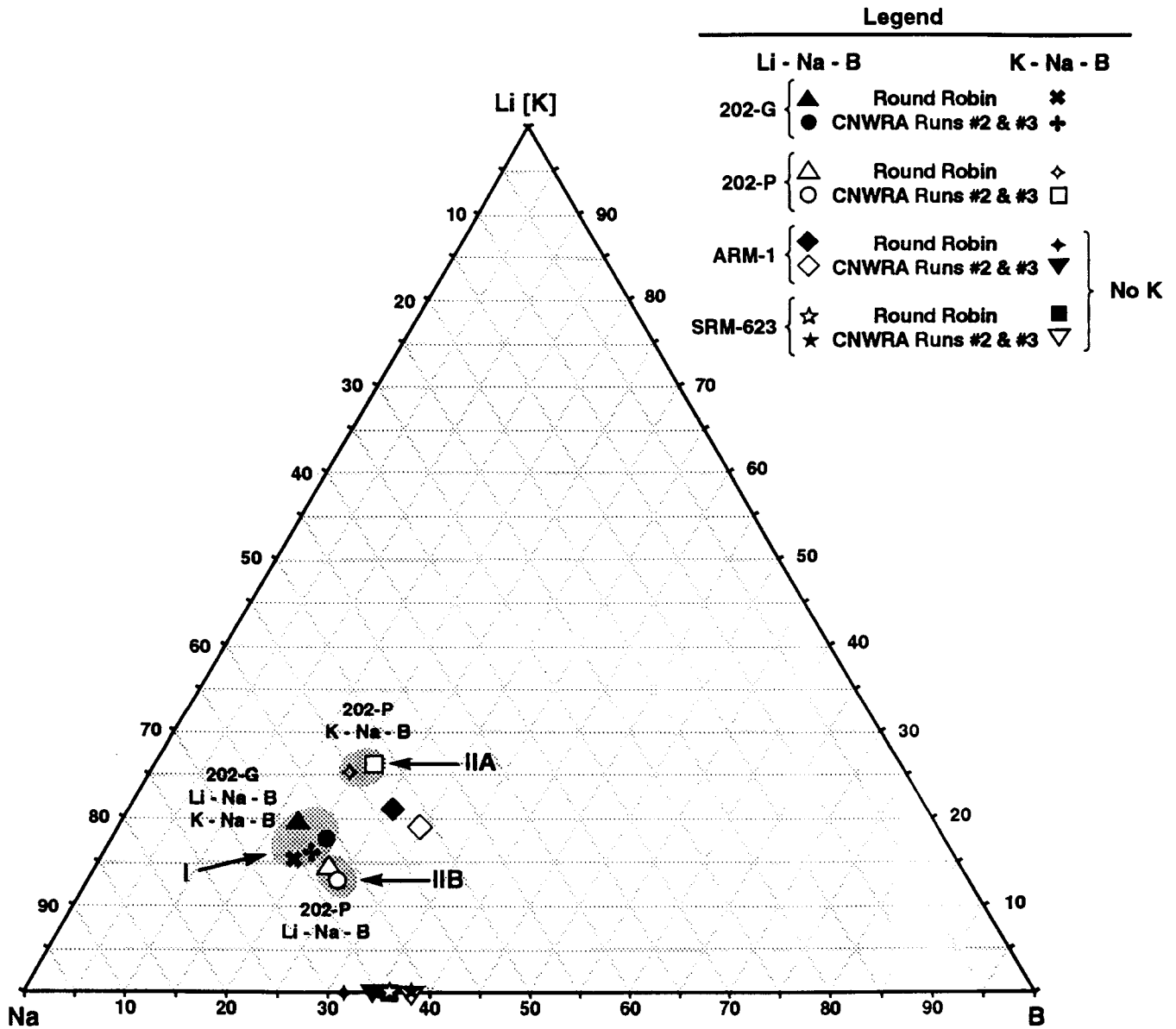


Figure 5-8. Coupled Releases of Li-Na-B and K-Na-B (Normalized to 100 mg/L for each Ternary) as a Function of Glass Type

#2 and #3). Comparison of the data for the two sets, Li-Na-B and K-Na-B, for SRL 202-P and SRL 202-G glasses show that for SRL 202-G glass (which is considered more durable than SRL 202-P), the data are more closely "lumped" together, as shown by domain I in Figure 5-8, while data for the SRL 202-P glass show a "split" distribution, data for Li-Na-B releases are separated from K-Na-B releases as shown by domains IIA and IIB in Figure 5-8. Whether such an empirical observation (split between the data points on Li-Na-B and K-Na-B plots) is a reliable indicator of the reduced durability of borosilicate glasses containing potassium or if some other correlation based on ternary release plots could be developed cannot be judged from the limited data generated in the CNWRA investigation. No trends for other glass types can be inferred from the ternary plot due to the limited data.

6 CONCLUSIONS

A comparison of the CNWRA and the round robin data indicate that the CNWRA results are generally within two standard deviations of the round robin mean. The CNWRA data, however, consistently are slightly lower than the round robin values. This difference has been attributed to the change in the procedure for preparing samples. The round robin samples were tested in unwashed condition (according to the draft PCT procedure current at the time the round robin was conducted) while the CNWRA crushed-glass samples were tested in the washed condition (which removed the crushing fines). Current information from the participants of the earlier round robin indicates that an increase of about 10 to 15 percent in the release of the highly leachable elements could be expected for unwashed samples, depending upon the amount of fines and the high solubility species in the glass. If one adjusts the data by 10 to 15 percent for the washing of the samples, the CNWRA results would generally be within one standard deviation of the round robin. Such a match is considered exceptionally good when one further realizes that for the CNWRA experiments all steps after the receipt of the solid glass samples were performed at the CNWRA and fresh specimens were prepared for each test run from the solid glass pieces. In contrast, for the round robin, all samples were prepared (crushed and sieved) by PNL from the same batches of glasses and were distributed to the participants for testing without any further processing (e.g., sieving, washing, or drying). All three round robin runs were made using samples from the same bulk glass which was prepared at the same time. There are other differences (within the allowed draft ASTM procedure) between the round robin and the CNWRA procedure, which might have contributed some to the difference in the results, two important being the sieving equipment and the type of leaching vessel which differed both in material of construction and configuration.

From the comparison of the CNWRA data with the round robin data, it is concluded that CNWRA PCT leaching protocols are calibrated with the other laboratories performing similar tests. The validation of the calibration is further strengthened by the match between the rank ordering using round robin and CNWRA data on glasses tested. Also, the CNWRA protocol leaching tests using draft ASTM procedure were able to discriminate between the two similar glasses (prepared from the same frit), namely, SRL 202-P and SRL 202-G, which have slightly different durability. The CNWRA results, just as those of the round robin, show that SRL 202-P is less durable than SRL 202-G. These two glasses were specially formulated to investigate the sensitivity of the PCT. The acceptability of the fabricated product (based on its consistency) will, however, be determined by DOE per the specifications of the WAPS (i.e., comparison with the releases of boron, sodium, and lithium) from the EA glass in a PCT (DOE, 1991). The relationship between the releases obtained in PCT and performance of the glass in a geological repository has not been determined as yet. Therefore, no conclusions can be drawn from the data presented regarding the performance of any of the four glasses tested under any repository conditions or their licensability under federal regulations as stated in Title 10 Code of Federal Regulations Part 60 (NRC, 1992).

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