Am/Cm Target Glass Durability Dependence on pH (U)

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At the Westinghouse Savannah River Company near Aiken, South Carolina, a process is being developed to safely vitrify all of the highly radioactive americium/curium (Am/Cm) material and a portion of the other fissile actinide materials stored on site. One goal of this campaign is to provide Oak Ridge National Laboratory with the excess Am/Cm so it can be recycled as opposed to simply disposing of it as waste. The vitrification will allow safe transportation of the Am/Cm to Oak Ridge as well as safe storage once it arrives. The Am/Cm Target glass being used in this project has been specifically designed to be extremely durable in aqueous environments while it can be selectively attacked by nitric acid to recover the valuable Am and Cm isotopes. Similar glass compositions could be used for storage and retrieval of other actinides on the WSRC site. Previous reports have presented the time, temperature, and compositional dependence of the Am/Cm glass durability. This paper will show results from a pH study on the Am/Cm Target glass durability. The data indicate that the Am/Cm Target Glass durability decreases as pH decreases from a neutral reading. These findings support the extraction of the valuable isotopes from the glass using nitric acid.

Introduction

Several experiments had been performed on the Am/Cm Target glass to examine its durability in terms of time and temperature. This report discusses some experiments to examine the pH dependence of the Am/Cm Target durability. All the experiments were performed using the Product Consistency Test developed at WSRC and discussed in the next section.

Product Consistency Test Description

Product Consistency Tests (PCT Test Method B) were performed on Am/Cm Target and Approved Reference Material[1] (ARM) glasses at WSRC Savannah River Technology Center (SRTC). The PCT's were done according to the requirements in the American Society for Testing and Materials (ASTM) Test Method C1285-94 *Determining Chemical Durability of Nuclear Waste Glasses: The Product Consistency Test (PCT)*[2] .

Tests were performed on the Am/Cm Target glasses in triplicate for various pH buffered solutions. Duplicate blanks were run for each pH buffer. Table I lists the elemental leachate concentrations for the Am/Cm Target glass where leachant pH's were 1, 4, 7, 10, and 13. Table I also lists a standard PCT run (90±2°C, DI H20 as leachate) on the Approved Reference Material (ARM) where pH ranges between 6 and 8. In Table I, BLK is the abbreviation for blank and ACT is short for Am/Cm Target glass. Table II lists the oxide compositions of the Am/Cm Target and ARM-1 glasses.

Each glass was ground using a Tekmar grinder with tungsten carbide blades. The ground glass was then sieved and a 100-200 mesh size collected in a beaker. The glasses were then washed by forcibly adding 15-20 ml of de-ionized water to the beaker and then decanting. This process was done three times. The glasses were also washed twice by forcibly adding 15-20 ml of de-ionized water, placing the beaker in an ultrasonic water bath for two minutes and then decanting. The process was repeated with ethyl alcohol. The glasses were then placed in a convection oven over night to dry.

Teflon® and stainless steel vessels were then prepared to receive the dried samples. First, the vessels and lids were cleaned by soaking them in 0.16M Nitric Acid (HNO_3) at 90°C ± 10°C for approximately one hour on a hot plate. These items were then rinsed with de-ionized water. The vessels were then soaked in fresh de-ionized water at 90°C ± 10°C for about an hour on a hot plate. The vessels were filled 80% full with de-ionized water (pH 5.0- 7.0), capped, and placed in a convection oven at 90°C ± 2°C for 16 hours. The pH values of the water after the 16 hour period were still between the pH 5.0 - 7.0 range. For the pH 1 and pH 4 tests, approximately 3.5 grams of each glass were then added to the cleaned Teflon® vessels and their weights recorded. Stainless steel vessels were not used for these two tests due to HCl in the

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[1]Mellinger, G. B., and J. L. Daniel, *Approved Reference and Testing Materials for use in Nuclear Waste Management Research and Development Programs*, U. S. DOE Report PNL-4955-2, Materials Characterization Center, Battelle Pacific Northwest Laboratory, Richland, WA, December, 1984.

[2] *ASTM C 1285-94*, Annual Book of ASTM Standards, American Society for Testing and Materials, Committee C-26 on Nuclear Fuel Cycle, Subcommittee C26.13 on Repository Waste Package Materials Testing, Volume 12.01, 1994.

pH 1 and pH 4 buffers. For the pH 7, pH 10 and pH 13 tests, approximately 1.5 grams of each glass were added to the cleaned stainless steel vessels and their weights recorded.

Table I. PCT Leachate Concentrations for Am/Cm Target (ACT) and ARM Glasses

(ppm)	Si	Pb	B	Al	Nd	Ba	Na	Li	Eu	La	Ce
BLK-1-PH1	5.70	<0.20	0.167	<0.15	<0.30	<0.01	1200	<0.015	<0.01	0.057	<0.15
BLK-2-PH1	5.51	<0.20	0.131	0.17	<0.30	0.017	1220	<0.015	<0.01	0.103	<0.15
ACT-1-PH1	110	1520	197	46.4	1140	233	1218	<0.30	77.0	2328	690
ACT-2-PH1	109	1530	197	47.3	1140	233	1208	<0.30	76.6	2313	684
ACT-3-PH1	108	1500	193	46.8	1130	228	1193	<0.30	77.2	2281	686
BLK-1-PH4	<0.05	<0.20	0.244	<0.15	<0.30	0.023	1.67	<0.015	<0.01	0.04	<0.15
BLK-2-PH4	<0.05	<0.20	0.147	<0.15	<0.30	0.022	0.334	<0.015	<0.01	<0.03	<0.15
ACT-1-PH4	86.7	6.20	66.7	1.36	186	37.3	0.927	0.016	16.O	253	70.6
ACT-2-PH4	87.8	2.91	88.0	1.07	202	43.5	1.14	0.019	19.O	229	68.0
ACT-3-PH4	82.3	3.01	80.8	1.04	205	43.3	1.08	0.017	19.6	233	69.4
BLK-1-PH7	0.183	<0.20	0.026	<0.15	<0.30	<0.01	0.216	<0.015	0.064	0.096	<0.15
BLK-2-PH7	0.401	<0.20	0.011	<0.15	<0.30	<0.01	0.138	<0.015	0.064	0.096	<0.15
ACT-1-PH7	3.74	<0.20	0.642	0.223	<0.30	0.678	0.171	<0.015	<0.01	<0.03	<0.15
ACT-2-PH7	7.03	<0.20	0.582	0.415	<0.30	0.123	0.447	0.033	<0.01	<0.03	<0.15
ACT-3-PH7	3.84	<0.20	0.698	0.311	<0.30	0.608	0.198	0.019	<0.01	<0.03	<0.15
BLK-1-PH10	3.43	<0.20	0.904	0.226	<0.30	<0.01	21.1	<0.015	0.064	0.096	<0.15
BLK-2-PH10	4.26	<0.20	0.573	2.43	<0.30	<0.01	21.1	<0.015	0.064	0.095	<0.15
ACT-1-PH10	33.8	<0.20	6.83	8.99	<0.30	0.044	21.0	0.058	<0.01	<0.03	<0.15
ACT-2-PH10	32.9	<0.20	6.23	8.56	<0.30	0.036	20.9	0.043	<0.01	<0.03	<0.15
ACT-3-PH10	36.1	<0.20	6.18	7.38	<0.30	0.036	27.1	0.078	<0.01	0.036	<0.15
BLK-1-PH13	0.701	<0.20	0.366	1.56	<0.30	<0.01	18.9	0.482	0.064	0.096	<0.15
BLK-2-PH13	0.804	<0.20	0.325	0.853	<0.30	<0.01	18.1	0.51	0.064	0.094	<0.15
ACT-1-PH13	129	50.3	25.3	44.5	<0.30	0.505	17.5	0.575	<0.01	<0.03	<0.15
ACT-2-PH13	128	51.5	25.8	44.7	<0.30	0.492	17.4	0.572	<0.01	<0.03	<0.15
ACT-3-PH13	132	50.7	27.0	44.9	<0.30	0.531	18.2	0.594	<0.01	<0.03	<0.15
ARM 1-PH7	66.5	<0.20	17.4	5.19	<0.30	0.020	40.2	15.6	<0.01	<0.03	<0.15
ARM 2-PH7	65.6	<0.20	17.4	5.18	<0.30	0.019	40.2	15.5	<0.01	<0.03	<0.15

Table II. Am/Cm Target and ARM-1 Glass Compositions

Oxide	ARM-1 Wt %	Am/Cm Target Wt %
Al_2O_3	5.59	6.24
B_2O_3	11.3	6.19
BaO	*	2.25
CaO	2.24	*
CeO_2	1.51	*
Ce_2O_3	*	8.22
Cs_2O	1.17	*
Eu_2O_3	*	0.72
Fe_2O_3	*	*
FeO	*	*
K_2O	*	*
La_2O_3	*	23.3
Li_2O	5.08	*
MgO	*	*
MnO	*	*
MnO_2	*	*
MoO_3	1.66	*
Na_2O	9.66	*
Nd_2O_3	5.96	11.62
PbO	*	13.48
SiO_2	46.5	27.97
TiO_2	3.21	*
ZnO	1.46	*
ZrO_2	1.8	*

*not applicable

An Orion pH meter was calibrated using 4, 7, and 10 pH buffers. The pH buffers 1, 4, 7, 10 and 13 were prepared and an initial pH was recorded as shown in Table III .

Table III. Preparation of pH Buffer Solutions

pH solution	Preparation	Initial pH
pH 1	Potassium Chloride/Hydrochloric acid	1.64
pH 4	Potassium Hydrogen Phthalate/Hydrochloric acid	4.07
pH 7	Potassium Orthophosphate di-H/Potassium Orthophosphate mono-H	7.17
pH 10	Potassium Orthophosphate/Potassium Orthophosphate mono-H	9.91
pH 13	Calcium Chloride/Potassium Hydroxide	12.48

For the pH buffer tests 1 and 4, approximately 35 grams of the buffer was added to each vessel and a total weight of the vessel, water, and glass was recorded. For the pH buffer tests 7, 10, and 13, approximately 15 grams of the buffer was added to each vessel and a total weight of the vessel, water, and glass was recorded. The vessels were capped and then placed in a Blue M convection oven at 90°± 2°C. The following day, the vessels were removed and checked to make sure that they were still tightly sealed. The oven temperature was monitored at half an hour intervals during the course of the study, using an Omega Thermocouple Thermometer.

After the seven day test period was complete, the vessels were taken out of the convection oven and allowed to cool. The vessels were weighed and the weight recorded. All of the samples had a weight loss of less than 1% over the course of the study. Each vessel was then uncapped and a pH taken. The final pH levels of the ARM glass standards were 10.22, 10.26, and 10.27. The final pH of the buffer pH 1 tests were 2.85, 2.89, and 3.13, buffer pH 4 tests were 5.02, 5.21, and 5.28, buffer pH 7 test were 6.55, 6.81, and 7.86, buffer pH 10 tests were 10.35, 10.40, and 10.41, and buffer 13 tests were 13.20, 13.21, and 13.24.

Sterilized syringes and filters were used to filter the leachate into pre-sterilized vials. A total of 20 ml was filtered into each vial and then 200 ml of ultrapure nitric acid was added. The samples were then submitted for elemental analyses on an Inductively Coupled Plasma-Atomic Emission Spectrometer (ICP-AES). Elements analyzed in the blanks, ARM glass standard, and Löffler glass leachates included silicon (Si), lead (Pb), boron (B), aluminum (Al), neodymium (Nd), barium (Ba), europium (Eu), lanthanum (La), and cerium (Ce). These leachate analyses are shown in Table I. In the next section, the durability of the glass is calculated from this data.

Durability Calculation

Data obtained from the PCT Tests were analyzed to determine the durability of Am/Cm Target glass as a function of pH. In the past, the concentrations of silica and boron have been examined since these elements leach the easiest and are therefore good indicators of a glass's durability. Since there is an interest in recovering the actinides in the Am/Cm Target glass, the concentrations of the actinide surrogates neodymium (Nd), lanthanum (La), and cerium (Ce) were also examined. First, the elemental release data was zeroed against the blanks to provide an unbiased representation of the leachate concentrations. Next, the normalized release of each element i was calculated using the following equation:

(1) $$NR_i = \frac{ppm_i}{1000 \bullet w_i}$$

where NR_i is the normalized release of element i in grams of glass dissolved per liter of solution, ppm_i is element i concentration in solution, and w_i is the weight fraction of element i in the glass. This calculation assumes the density of the solution is about that of water or 1 gram/milliliter. For the Am/Cm Target and ARM glasses, the weight fraction of each of the elements examined are given in Table IV. It is common practice to look at the log-normal concentration of glass leachates which is simply the log of the NR values from equation 1. Table V shows the raw ppm releases along with the normal (NR) and log-normal (LNR) releases for the Am/Cm Target glass data that were analyzed for the series of pH experiments discussed earlier.

Table IV. Weight Fraction of Elements in Am/Cm Target and ARM Glasses

Glass	Si	B	Nd	La	Ce
Am/Cm Target	0.120	0.0164	0.0841	0.144	0.0605
ARM	0.224	0.0361	0.0526	0	0.0127

The data in Table V is plotted in Figures 1 through 6. The lines in the figures are just for illustration of the general shape of the data. Looking at Figures 1 through 3, one can see that as the pH moves away from a neutral position, the durability decreases as evidenced by the normalized boron release going from about 0.04 grams of glass per liter at a pH around 7 to about 12 grams of glass per liter at a pH around 3. Figures 4 through 6 show a similar type of behavior for the actinide surrogates in the Am/Cm Target glass. As the pH decreases from a neutral value, the release of the actinide surrogate jumps from below the detectable limit to about 14 grams of glass per liter. These results support the plan to use nitric acid to extract the valuable actinide isotopes from the Am/Cm Target glass.

Table V. Am/Cm Target Releases versus pH

Sample	pH	Si ppm	NR(Si) g/L	LNR(Si)	B ppm	NR(B) g/L	LNR(B)	Nd ppm	NR(Nd) g/L	LNR(Nd)	La ppm	NR(La) g/L	LNR(La)	Ce ppm	NR(Ce) g/L	LNR(Ce)
Am/Cm Target	2.85	104.4	0.8736	-0.0587	196.9	12.00	1.0790	1139.7	13.56	1.1321	2327.9	16.14	1.2080	689.85	11.397	1.0568
	2.89	103.4	0.8652	-0.0629	196.9	12.00	1.0790	1139.7	13.56	1.1321	2312.9	16.04	1.2052	683.85	11.298	1.0530
	3.13	102.4	0.8569	-0.0671	192.9	11.75	1.0701	1129.7	13.44	1.1283	2280.9	15.82	1.1991	685.85	11.331	1.0543
	5.02	86.65	0.7251	-0.1396	*	*	*	185.7	2.209	0.3441	253.0	1.754	0.2441	70.45	1.164	0.0659
	5.21	87.75	0.7343	-0.1341	87.8	5.351	0.7284	201.7	2.399	0.3800	229.0	1.588	0.2008	67.85	1.121	0.0496
	5.28	82.25	0.6883	-0.1622	80.6	4.912	0.6913	204.7	2.435	0.3864	233.0	1.615	0.2083	69.25	1.144	0.0584
	6.55	3.448	0.0289	-1.5398	0.6235	0.0380	-1.4203	0	0	*	0	0	*	0	0	*
	6.81	*	*	*	0.5635	0.0343	-1.4642	0	0	*	0	0	*	0	0	*
	7.86	3.548	0.0297	-1.5274	0.6795	0.0414	-1.3829	0	0	*	0	0	*	0	0	*
	10.35	29.96	0.2507	-0.6009	6.092	0.3712	-0.4304	0	0	*	0	0	*	0	0	*
	10.40	29.06	0.2431	-0.6141	5.492	0.3346	-0.4754	0	0	*	0	0	*	0	0	*
	10.41	32.26	0.2699	-0.5688	5.442	0.3316	-0.4794	0	0	*	0	0	*	0	0	*
	13.20	128.2	1.073	0.0307	24.95	1.521	0.1820	0	0	*	0	0	*	0	0	*
	13.21	127.2	1.065	0.0273	25.45	1.551	0.1907	0	0	*	0	0	*	0	0	*
	13.24	131.2	1.098	0.0407	26.65	1.624	0.2107	0	0	*	0	0	*	0	0	*
ARM	10.26	66.21	0.2959	-0.5289	17.38	0.4811	-0.3178	0	0	*	*	*	*	0	0	*
	10.27	65.31	0.2919	-0.5348	17.38	0.4811	-0.3178	0	0	*	*	*	*	0	0	*

*not applicable

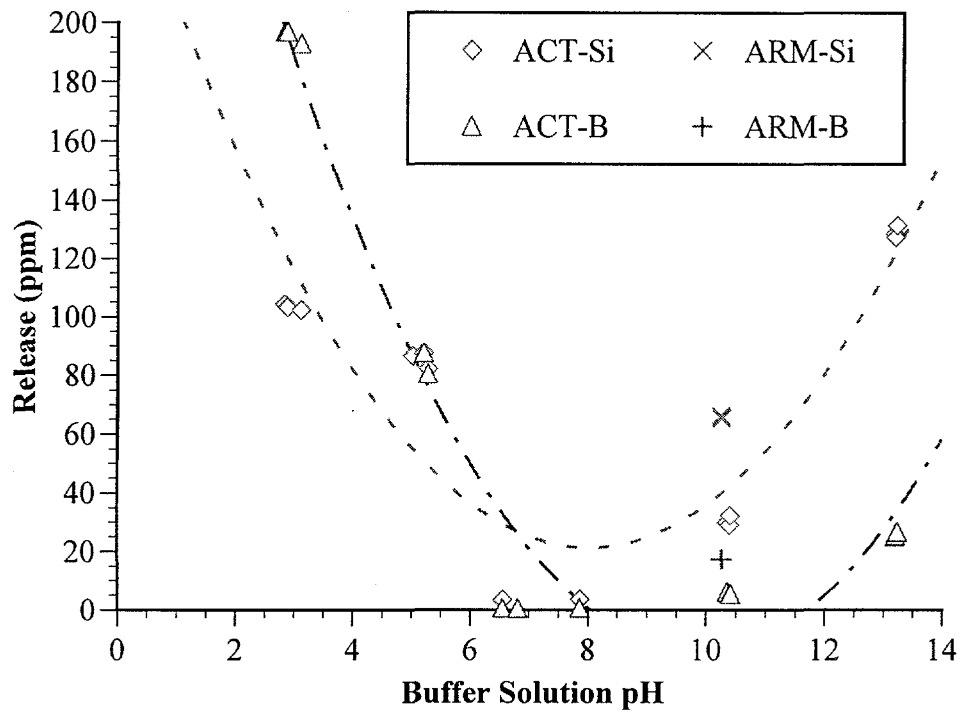

Figure 1. Am/Cm Target (ACT) silica and boron leachate concentrations for different pH buffered solutions.

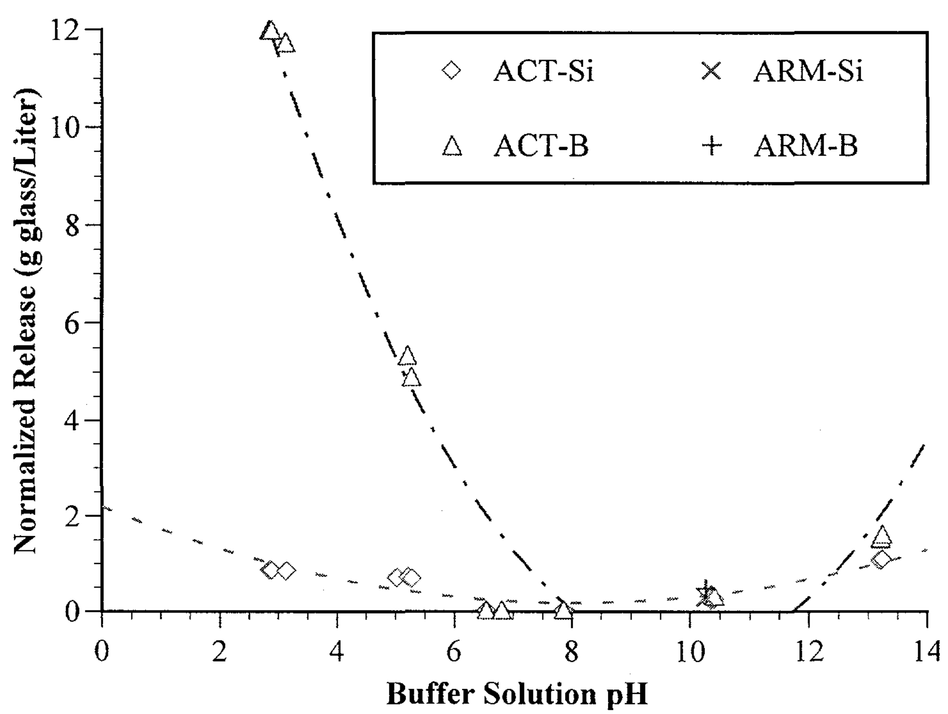

Figure 2. Am/Cm Target (ACT) silica and boron normalized elemental releases for different pH buffered solutions.

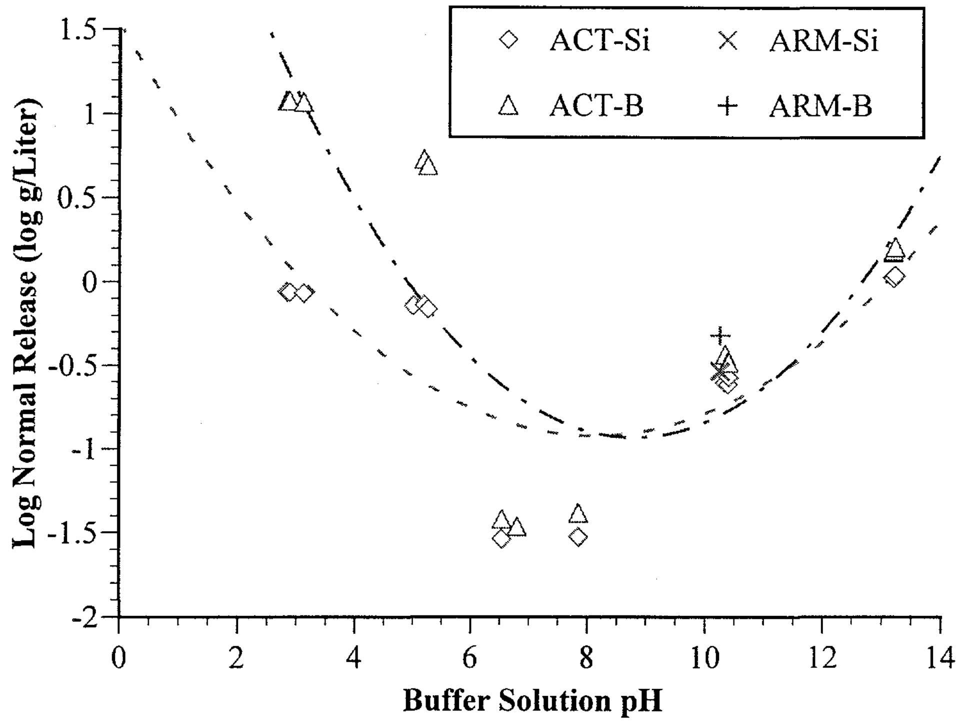

Figure 3. Am/Cm Target (ACT) silica and boron log normal elemental releases for different pH buffered solutions.

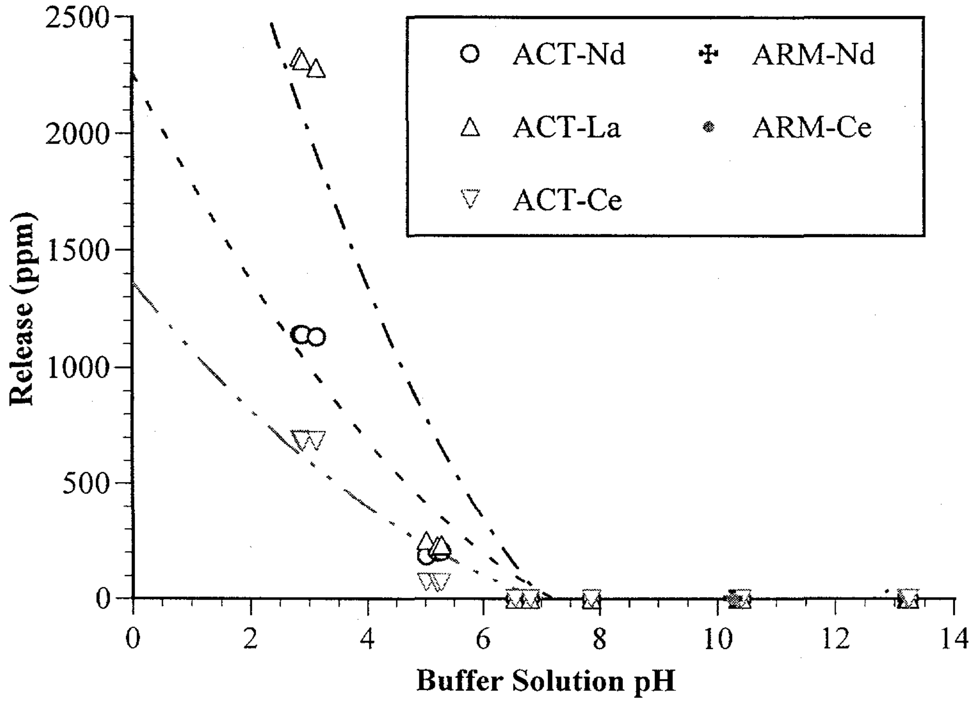

Figure 4. Am/Cm Target (ACT) actinide surrogate leachate concentrations for different pH buffered solutions.

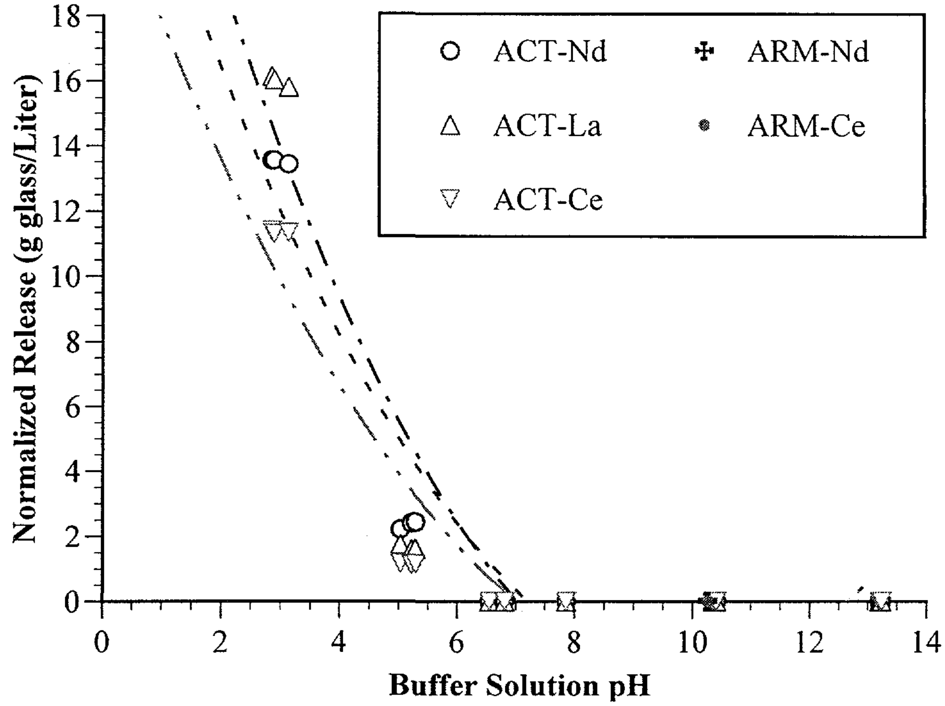

Figure 5. Am/Cm Target (ACT) actinide surrogate normalized elemental releases for different pH buffered solutions.

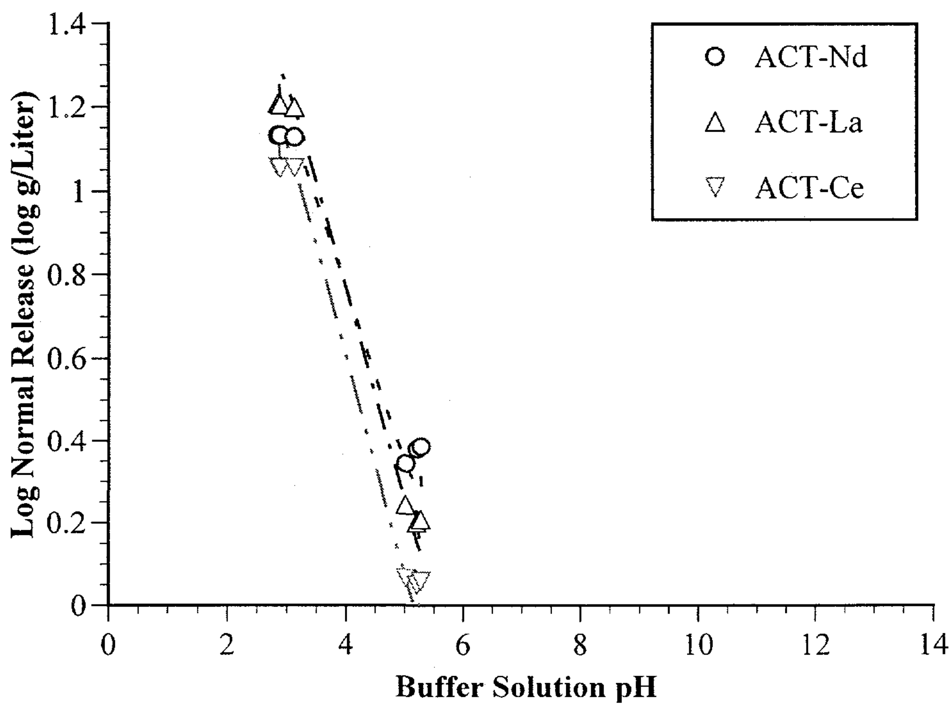

Figure 6. Am/Cm Target (ACT) actinide surrogate log-n ormal elemental r eleases for different pH buffered solutions.

Conclusions

These experimental studies on Am/Cm Target glass have shown that its durability is strongly dependent on pH. As the pH of the solution decreases away from a neutral pH, the elemental releases increase orders of magnitude. Looking at the boron releases, the dissolution is around 0.04 at a neutral pH and rapidly rises to approximately 12 grams of glass dissolved per liter of solution at a pH around 3. The releases of the actinide surrogates (Nd, La, Ce) exhibit the same type of behavior, where the normalized release is below the detectable limit around a neutral pH and is around 14 grams of glass dissolved per liter of solution around a pH of 3. These findings support using the Am/Cm Target glass for storage of the actinides due to its high durability in aqueous or semi-neutral environments. These results also support the idea of using nitric acid to selectively extract the valuable isotopes from the Am/Cm Target glass. Studies on nitric acid extraction of the real isotopes from the Am/Cm Target glass have just been completed. Once that data becomes available, this report will be revised to include the new information.