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LEACHING OF ACTINIDE-DOPED NUCLEAR WASTE GLASS IN A TUFF-DOMINATED SYSTEM

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ABSTRACT

A laboratory leaching test has been performed as part of a project to evaluate the suitability of tuff rocks at Yucca Mountain, Nevada, as a site for a high-level nuclear waste repository. Glass samples were placed in water inside tuff vessels, and then the tuff vessels were placed in water inside Teflon containers. Glass-component leach rates and migration through the tuff were measured for samples of the ATM-8 actinide glass, which is a PNL 76-68 based glass doped with low levels of ^{99}Tc, ^{237}Np, ^{238}U, and ^{239}Pu to simulate wastes. Disc samples of this glass were leached at 90°C for 30, 90, and 183 days inside tuff vessels using a natural groundwater (J-13 well-water) as the leachant. Some samples were held by 304L stainless steel supports to evaluate the effect of this metal on the release rate of glass constituents. At the end of each leaching interval, the J-13 water present inside and outside the rock vessel was analyzed for glass components in solution.

On the basis of these analyses, boron, molybdenum, and technetium appear to migrate through the rock at rates that depend on the porosity of each vessel and the time of reaction. The actinide elements (uranium, neptunium, and plutonium) were found only in the inner leachate. Sodium, silicon, and strontium are present in the rock as well as in the J-13 water, and the addition of these elements from the glass could not be determined. Normalized elemental mass loss values for boron, molybdenum, and technetium were calculated using the combined concentrations of the inner and outer leachates and assuming a negligible retention on the rock. The maximum normalized release was 2.3 g/m^2 for technetium. Boron, molybdenum, technetium, and neptunium were released linearly with respect to each other, with boron and molybdenum released at about 85% of the technetium rate, and neptunium at 5-10% of the technetium rate. Plutonium was found at low levels in the inner leachate but was strongly sorbed on the steel and Teflon supports. Neptunium was sorbed to a lesser extent. Future analysis of the tuff vessels will determine whether the actinides were strongly sorbed on the surface of the tuff rock.

INTRODUCTION

The Nevada Nuclear Waste Storage Investigations Project, NNWSI, is evaluating the tuffaceous rocks of Yucca Mt., Nevada, for suitability as a site for a high-level nuclear waste repository. As part of that project, Lawrence Livermore National Laboratory is responsible for the design of the waste package and assessment of its performance in the repository. One form in which high-level waste will be stored is borosilicate glass cast in stainless steel containers; waste of this form will be produced by the Defense Waste Processing Facility at the Savannah River Plant, and by the West Valley Demonstration Project at West Valley, New York.[1]

We have performed an experiment to evaluate the leaching of the ATM-8 glass in a water-saturated tuff environment and to study the migration of glass components in solution through tuff rock. The tuff vessel experiment is a static leaching experiment in which the glass is held inside a closed tuff vessel during the reaction time. Similar tests[2,3] have been conducted using both radioactive and non-radioactive glass, and the results suggest that the tuff and J-13 ground water environment is less corrosive towards glass than

J-13 or deionized water alone. Our results corroborate that information in more detail, particularly with respect to boron, molybdenum, and technetium.

EXPERIMENTAL

The glass specimens were nominally 3 mm thick and 10 mm in diameter;[4] each disc weighed approximately 0.7 g and had a geometric surface area of 2.6 cm^2. Three of these discs were used in each vessel. The chemical composition of the ATM-8 glass is listed in Table I. One of the two analyses shown in this table was done at LLNL, and the other one was compiled by MCC.[4] The reference composition used in all calculations in this paper is that obtained at LLNL. Some of the differences in composition, as shown in Table I, may be due to the fact that the glass material analyzed at LLNL came from a composite sample of crushed glass different from the samples analyzed at MCC. If the values for elements not analyzed at LLNL are added to the LLNL total, the result is 100.38%.

The tuff vessels, such as the one shown in Fig. 1(A), were fabricated at Lawrence Livermore National Laboratory using tuff rock from Fran Ridge, Nevada Test Site, a surface outcrop of the Topopah Springs tuff. The vessels were cored from large samples which did not contain large vugs or altered cracks. Each finished vessel was approximately 7 cm in length and 5 cm in diameter with a core-barrel 6 cm in length and 2.5 cm in diameter; the lid was 1 cm thick. The vessels were cleaned prior to use to remove surface salt contamination.

TABLE 1.

COMPOSITION OF ATM-8 GLASS

OXIDE	MCC*(a) (wt%)	MCC STANDARD DEVIATION	LLNL(d) (wt%)
Ag_2O	N.A.	--	N.A.
Al_2O_3	1.06	0.05	1.13
B_2O_3	8.18	0.28 (b)	8.53
BaO	0.61	0.02	0.54 (e)
CaO	2.13	0.06 (b)	2.58
CdO	<DL, 0.005	--	N.A.
CeO_2	0.11	0.03	<D.L., 0.05
Cr_2O_3	0.46	0.02	N.A.
Cs_2O	N.A.	--	0.97 (e)
Dy_2O_3	0.01	0.00	N.A.
Eu_2O_3	<DL, 0.01	--	N.A.
Fe_2O_3	8.18	0.24	8.96
Gd_2O_3	<DL, 0.05	--	N.A.
K_2O	N.A.	--	N.A.
La_2O_3	4.07	0.15	4.88 (e)
MgO	0.16	0.01	0.14
MnO2	0.06	0.01	N.A.
MoO_3	1.98	0.04	2.24
Na_2O	12.2	0.20 (b)	13.09
Nd_2O_3	1.66	0.06	1.55 (e)
NiO	N.A.	--	0.26
P_2O_5	0.57	0.07 (b)	N.A.
PdO	0.37	0.10 (c)	N.A.
Rh_2O_3	N.A.	--	N.A.
RuO_2	0.58	0.10	N.A.
SiO_2	57.8	0.70 (b)	N.A.
Sm_2O_3	<DL, 0.05	--	N.A.
SrO	0.47	0.01	0.50
TeO_2	<DL, 0.1	--	N.A.
TiO_2	2.61	0.10	2.79
Y_2O_3	<DL, 0.1	--	N.A.
ZnO	4.37	0.12	4.46
ZrO_2	1.99	0.05	2.70
Radioactive Const'tuents			
NpO_2	0.38	0.02 (b)	0.38 (f)
PuO_2	0.11	0.11 (b)	0.097 (g)
Tc_2O_7	0.18	0.01 (b)	0.19 (e)
UO_2	4.24	0.07 (b)	4.15
Totals	95.36		60.08

(d) Plutonium Ratios:
240/239=0.0769
241/239=0.0031
242/239=0.000565

(a) Based on analyses of 16 specimens taken from 9 bars unless otherwise specified. Standard deviations are for an individual analysis.
(b) From analyses of 4 specimens taken from 3 different bars.
(c) From analyses of 12 specimens taken from 3 different bars.
(d) ICP analysis
(e) XRF analysis
(f) Gamma spectroscopy
(g) Alpha spectroscopy
(h) Mass spectroscopy analysis
N.A. - not analyzed
* PNL - 2577-8
<DL - Below the detection limit indicated

TABLE II

VESSEL PERMEABILITY

Vessel No.	Time (d)	Permeability (ud)	Tuff Description
1	30	1800	Large area of vapor phase alteration and discoloration
8	30	300	Large lithic fragment included
16	30	12	Large area of vapor phase discoloration
11	30	580	Uniform welded tuff
12	30	12	Uniform welded tuff
7	90	1400	Large area of vapor phase alteration
3	90	28	Uniform welded tuff, one healed fracture
10	90	78	Small area of vapor phase discoloration
2	90	100	Uniform welded tuff
4	90	18	Small area of vapor phase discoloration and two healed fractures
13	183	1100	Large area of alteration, one open vug
14	183	28	Small discolored area
5	183	51	Uniform welded tuff
6	183	56	Large discolored area
9	183	76	Large discolored area
15	183	40	Small discolored area

Sixteen vessels were used in the experiment and each was tested for its permeability before any work was begun. The permeability constants range from 12 μd to 1900 μd and are shown in Table II, along with a brief description of each vessel.

Stainless steel or Teflon supports were used to hold the samples in position during the leaching phase. The stainless steel supports were fabricated from 2.2 x 2.2 cm squares of 0.16 cm thick 304L stainless steel coupons. The corners of the squares were bent downward to allow approximately 0.5 cm of space between the top of the support and the bottom of the vessel. Furthermore, the surface of the support was perforated with nine 0.318 cm-diameter holes to allow a free path for water circulation around the glass discs. The Teflon supports were 0.3 cm thick screens purchased from Savillex Corporation (Part No. 465C). Both support types are pictured in Fig. 1(B).

The components of the leaching experiment are shown in Figure 1(B) and the configuration is shown in Fig. 1(C). Because of space restriction inside the tuff vessel, the three glass discs lay flat next to each other on top of either a stainless steel or Teflon support which rested at the base of each vessel. A known amount of J-13 water (pre-equilibrated for two weeks at 90°C with each individual vessel), based on the surface area of the glass discs and a surface area to volume ratio of 0.39 cm^{-1}, was added to the inside of the vessel. The vessel was covered with its loose cap and placed in a 500 cm^3 Teflon jar; then a known amount of pre-equilibrated J-13 water based on the height of the volume inside the vessel, was carefully added to the annular space between the exterior of the vessel and the Teflon jar. This jar was screw-capped and the entire package was weighed to record a gross starting weight.

Blank samples were also assembled to be run concurrently with the glass samples. These blanks consisted of the tuff vessel, pre-equilibrated J-13 water inside and outside the vessel, and a stainless steel or Teflon

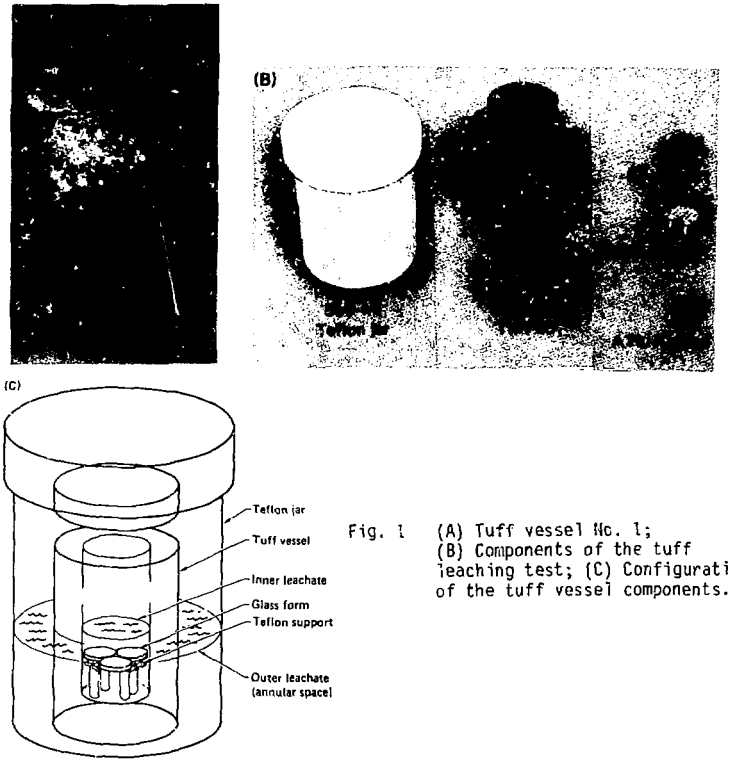

Fig. 1 (A) Tuff vessel No. 1; (B) Components of the tuff leaching test; (C) Configuration of the tuff vessel components.

support. The average of the inner and outer elemental concentrations of these blanks for each time interval was used as the blank correction on the glass samples.

When both the inner and outer leachates were removed from their respective containers at the end of 30, 90, and 183 days, the pH of each solution was measured and a 1 cm^3 aliquot from each sample was removed for anion analysis. The remaining portions were acidified with nitric acid in clean Teflon containers and placed in a 90°C oven for 24 hours. At the conclusion of this period, aliquots of the solutions were removed for cation analyses with a Jarrell Ash Inductively Coupled Plasma (ICP) Spectrometer.

Two elements, cesium and uranium were analyzed using x-ray fluorescence. Technetium was measured by beta counting. Neptunium and plutonium were measured by alpha counting.

The normalized elemental mass loss, NL_i, was calculated for boron, molybdenum, technetium, neptunium, and plutonium. These results are expressed in grams of dissolved glass per square meter of the geometric surface area of the specimen.

The boron, molybdenum, and technetium values were calculated using the formula:

$$NL_i = \frac{(C_x)(V)}{(f_x)(SA)} \quad (1)$$

where C_x = concentration of element x in the leach solution, g/cm^3
V = volume of leach solution, cm^3
f_x = mass fraction of element x in the unleached specimen
SA = specimen surface area, m^2

In this experiment, the total mass of element x in the leach solution was obtained from the concentration inside the tuff vessel and the concentration in the annular space.

The neptunium and plutonium elemental mass loss values were calculated from the formula:

$$NL_i = \frac{(a_x)(V)}{(a_o)(SA)} \quad (W_o) \quad (2)$$

where a_x = activity of isotope x in the leach solution, dpm/cm^3
a_o = original activity of isotope x in the unleached specimen, dpm
W_o = original mass of the specimen, g
V = as defined in (1)
SA = as defined in (1).

RESULTS AND DISCUSSION

Permeability Measurements

All sixteen tuff vessels were individually measured for permeability. The calculated constants shown in Table II exhibited a large range, from 12 to 1900 μd. The more permeable vessels developed localized flow patterns, with the higher leakage paths associated with specific altered areas or inclusions. This alteration can enhance permeability by opening pathways or can decrease it by precipitation of secondary phases. Major areas of leakage always corresponded to altered areas but not all of the altered areas leaked as observed during the permeability tests.

The Topopah Springs welded tuff frequently has inclusions of other tuffs, which were picked up during magma transport as solid pieces. In the vessels fabricated for this experiment, there are many gray lithic fragments of this type. Most are small (<1cm) but vessel No. 8 contains a large fragment making up about 40% of the vessel. This vessel is distinct in the final pH and release rates, apparently because of the different properties of this lithic fragment. Some of the variability seen in the other vessels may also be due to their smaller lithic fragments.

Blank Samples

Four blank samples were run concurrently with the vessels containing the glass specimens. The "blanks" were assembled in the same manner as the real samples but did not contain glass. The objective of running control samples was to obtain elemental concentrations which could be subtracted from the sample solutions containing the leached glass components. Because of the

limited supply of vessels, only single blanks were run with the 30-day and the 90-day samples whereas duplicate blanks were run with the 183-day samples. The inner and outer leachate concentrations were averaged and the average value was then used as a blank correction; in the case of the 183-day samples all four values were averaged to obtain a single correction value. Boron and molybdenum corrections were applied in the treatment of the data as discussed later in this report; the other elements discussed had blanks of zero.

pH Measurements

pH measurements were made in each of the leachate solutions soon after the conclusion of the leaching periods. The pH readings are tabulated in Table III as a function of the reaction time and the presence of steel or Teflon inside the vessel. Also shown in the same table are pH readings of the "blank" solutions.

The pH of the inner and outer leachates are approximately the same, suggesting that the presence of the glass inside the vessels has little effect on the final pH of the solution. The fact that the system may be dominated by the tuff and the J-13 groundwater is further confirmed by the pH readings taken on the "blanks". The average value of the eight readings corresponding to the four blank samples is 8.87 ± 0.25, which is in the same range as the samples containing glass.

Measurements were also made on the starting solutions which originated from the separate two-week equilibrations of the vessels prior to the leaching phase. The average pH value of these 16 solutions (listed in Table III) is 8.48 ± 0.18, which is slightly lower than the pH values of the leachates at the end of each leaching period. These solutions were returned to the vessels for the leaching phase.

TABLE III

pH MEASUREMENTS

VESSEL No.	SUPPORT TYPE	REACTION TIME	INITIAL pH	FINAL pH INNER	FINAL pH OUTER
1*	Teflon	30	8.22	8.42	8.77
8	Steel	30	8.48	8.20	8.94
16	Steel	30	8.33	8.56	8.94
11	Teflon	30	8.55	8.52	9.02
12	Teflon	30	8.48	8.64	9.00
7*	Steel	90	8.31	8.90	8.66
3	Steel	90	8.59	8.92	9.11
10	Steel	90	9.44	8.74	8.97
2	Teflon	90	8.24	9.02	8.94
4	Teflon	90	8.93	9.12	9.30
13*	Steel	183	8.45	8.92	9.13
14*	Teflon	183	8.60	8.95	9.17
5	Steel	183	8.48	8.62	8.73
6	Steel	183	8.37	8.95	8.98
9	Teflon	183	8.54	8.78	9.00
15	Teflon	183	8.68	9.11	9.24

NOTE: Average Initial pH = 8.48 +/- 0.18.
* "Blank" Samples

Figure 2 shows the pH results as a function of time for the inner leachates. The pH follows the same trends and values as seen when equilibrating tuff alone[5] and the blanks fall within the sample range for each time period. Figure 3 shows the final inner pH as a function of the initial pH in the two-week equilibration. If the tuff alone controls the pH, it might be expected that there would be a positive correlation. There is some evidence of this occurrence; samples 15 and 4 had both the highest initial and final pH. The remaining samples fall in a fairly tight cluster. Sample 8 appears to behave differently because of the large lithic fragment it contains. If we ignore this anomaly, the 30-day samples show a linear, positive trend as do the combined 90 and 183-day samples.

When 76-68 based glasses such as ATM-8 are tested in deionized water, the pH equilibrates in the range 9.5 to 10.[6] The lower pH values in this study are due to the combined buffering effects of the tuff rock and the carbonate dissolved in J-13 water. The range of pH values is indicative of the complexity of the interaction of these buffering agents with the components released by the glass.

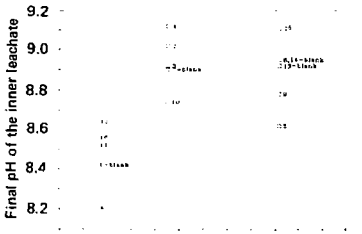

Fig. 2 pH of the leachate inside the tuff vessel as a function of reaction time. (Sample Nos. are next to data points.)

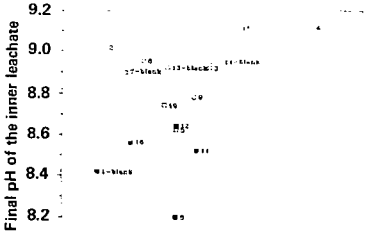

Fig. 3 Final pH inside the tuff vessel as a function of initial pH. (Sample Nos. are next to data points. Solid symbols represent 30-day samples.)

Boron, Molybdenum, and Technetium

The boron, molybdenum and technetium concentrations in ppm are shown in Table IV. These results, along with the volumes of the leachates, were then used to calculate a) the total amounts inside and outside the vessel and b) the fraction of the total dissolved element in the annular (outer) space.

In the 30-day samples, the boron concentrations in the annular space are 88, 44, 73, and 45% of the total boron released into solution for the four vessels with permeability constants of 300, 12, 590, and 12 μd respectively. The permeability effect is more evident in the case of technetium; here, the concentrations in the annular space are 70, 6, 63 and 6% for the same four vessels. In the case of molybdenum, the concentrations for the two samples with the higher permeability constants (300 and 590 μd) are 84 and 52% respectively. The molybdenum concentrations in the two samples with permeability constants of 12 μd were not calculated because the measured concentrations in the outer leachates were at the same level as the blank (control) samples.

TABLE IV.
B, Mo, Tc FRACTIONS IN ANNULAR SPACE

VESSEL NO.	PERM (ud)	REACTION TIME(d)	FINAL WEIGHT(g) INNER	OUTER	BORON PPM Inner	Outer	Fraction	MOLYBDENUM PPM Inner	Outer	Fraction	TECHNETIUM PPM Inner	Outer	Fraction
8	300	30	10.37	169.9	0.09	0.04	0.68	0.03	0.01	0.84	0.0053	0.00078	0.70
11	12	30	17.73	165.4	0.60	0.05	0.44	0.21	-0.01		0.022	0.00016	0.66
11	590	30	8.26	172.9	0.31	0.04	0.73	0.19	0.01	0.52	0.031	0.0025	0.63
12	12	30	17.14	163.9	0.59	0.05	0.65	0.26	-0.01		0.028	0.00018	0.06
3	28	90	17.52	159.4	1.19	0.07	0.35	1.01	0.03	0.21	0.077	0.0046	0.35
10	78	90	15.0	162.5	0.44	0.02	0.33	0.22	0.01	0.33	0.018	0.0013	0.44
2	100	90	14.50	159.6	0.52	0.07	0.60	0.45	0.04	0.51	0.028	0.0051	0.66
4	18	90	14.86	157.2	0.87	0.06	0.42	0.73	0.03	0.30	0.058	0.0037	0.40
5	51	183	15.69	156.5	0.55	0.16	0.74	0.47	0.05	0.51	0.035	0.0071	0.67
6	56	183	14.25	158.3	0.26	0.07	0.75	0.18	0.01	0.38	0.014	0.0023	0.68
9	76	183	16.32	157.2	0.48	0.18	0.78	0.41	0.06	0.58	0.027	0.007	0.72
15	40	183	14.32	157.2	0.47	0.13	0.75	0.50	0.05	0.52	0.033	0.0061	0.67

In the 90-day samples, the permeability constants of the four vessels range from 18 to 100 μd. Although, this spread is not as severe as in the case of the 30-day samples, again the permeability effect in the migration of the three elements, across the tuff is evidenced in sample 2 (100 μd). The concentration of the total boron, molybdenum, and technetium released in solution in the annular space is 60, 51, and 66% respectively whereas the concentrations for the other three vessels with lower permeability range from 21 to 44%.

In the 183-day samples, the permeability effect is not noticeable either because of equilibration due to the longer reaction time or because the permeability constants of the four vessels are clustered between 40 and 76 μd. Thus, the annular concentrations are likewise clustered together with boron showing the highest values (74 to 78%), then technetium (67 to 72%), and, last, molybdenum (38 to 58%).

Uranium and Cesium

Uranium and cesium analyses were performed on all leachates. Uranium was detected only in the inner leachates of the 90-day and 183-day samples; the concentrations in the outer leachates were below the limit of detection of the analytical method. Similarly, the cesium results were all below the limit of detection of the analytical method. Consequently, migration of uranium and cesium across the tuff is not evident.

Plutonium and Neptunium

Plutonium and neptunium were detected only in the inner leachates. The concentrations in the outer leachates were all below limit of detection. Measurements were also made on the steel and Teflon supports which were used inside the vessels. These data are shown in Table V. The plutonium activity found in solution is low and non-systematic; the residual activity found on the supports was significantly larger and it appears to be much more strongly associated with the steel supports than with the Teflon supports. It is not entirely surprising that this residual activity is so large since the pH of the leachates is approximately 9.0 at the end of each reaction period, and plutonium tends to adsorb or precipitate under this condition.

The neptunium activity found in solution is somewhat larger than the plutonium activity but still non-systematic; the residual activity on the supports varies greatly from sample to sample. The amount sorbed on the Teflon is small and non-systematic, that on the steel shows a good linear relationship with the activity in solution.

TABLE V

NEPTUNIUM-237 and PLUTONIUM-239 DATA

			Inner Leachate		Outer Leachate		Supports	
			dpm		dpm/0.1cm3		dpm	
Sample	Time	Support	Np-237	Pu-239	Np-237	Pu-239	Np-237	Pu-239
8	30	S.Steel	23 +/- 8%	9 +/- 13%	<0.1	<0.02	29	198
16	30	S.Steel	144 +/- 3%	4 +/- 17%	<0.1	<0.02	38	619
11	30	Teflon	87 +/- 4%	1 +/- 29%	<0.1	<0.02	16	207
12	30	Teflon	104 +/- 5%	12 +/- 33%	<0.1	<0.02	16	322
3	90	S.Steel	623 +/- 2%	18 +/- 9%	<0.1	<0.02	191	4300
10	90	S.Steel	140 +/- 4%	8 +/- 2%	<0.1	<0.02	22	1000
2	90	Teflon	220 +/- 3%	4 +/- 16%	<0.1	<0.02	19	203
4	90	Teflon	386 +/- 5%	5 +/- 12%	<0.1	<0.02	21	409
5	183	S.Steel	330 +/- 1%	12 +/- 6%	<0.1	<0.02	108	5920
6	183	S.Steel	96 +/-2%	4 +/- 10%	<0.1	<0.02	20	2700
9	183	Teflon	245 +/- 2%	27 +/- 5%	<0.1	<0.32	11	295
15	183	Teflon	273 +/- 1%	9 +/- 6%	<0.1	<0.02	28	381

Note: Radiochemical Method Inner Sample 5: Np=353 dpm (1%), Pu=9 dpm (13%)
Radiochemical Method Inner Sample 15: Np=302 dpm (1%), Pu=? dpm (12%)
Radiochemical Method Outer Samples 5,6,9,15: Np=<0.1, Pu=<0.02 dpm

Normalized Elemental Mass Loss

Normalized elemental mass loss values were calculated for boron, molybdenum, technetium, neptunium, and plutonium. These are shown in Table VI. The boron, molybdenum, and technetium values were calculated using the sum of the inner and outer leachate amounts; neptunium and plutonium were found in the inner leachates only. The technetium normalized mass loss values are the highest. When these values are plotted as a function of time as shown in Figure 4, the trend is that of initial rapid release followed by slower release. This trend has been observed previously in static leach testing.[2] The boron and molybdenum data behave very much like the technetium data. There also seems to be a similarity between the pattern of mass dissolution rate of technetium as a function of time and the pH pattern of the inner leachates shown in Figure 2. This similarity is an indication of the strong correlation between pH and the net breakdown of the glass, which would normally be expected due to the gradual increase in pH as the glass releases basic components.[6] In this system, the pH appears to be controlled by the tuff vessel, yet the glass release is still strongly correlated to the pH (Figure 5).

TABLE VI

NORMALIZED MASS LOSS: g glass/m²

SAMPLE NO.	TIME (d)	TYPE SUPPORT	PERM (ud)	B	Mo	Tc	Pu	Np	INNER pH
8	30	Steel	300	0.38	0.18	0.21	9.40E-05	6.00E-03	8.2
16	30	Steel	12	0.92	0.32	0.45	3.80E-05	3.90E-02	8.56
11	30	Teflon	590	0.47	0.29	0.75	1.00E-05	2.30E-02	8.52
12	30	Teflon	12	0.90	0.38	0.56	1.40E-04	2.70E-02	8.64
3	90	Steel	28	1.54	1.92	2.27	1.90E-04	1.60E-01	8.92
10	90	Steel	78	0.48	0.43	0.51	8.60E-05	3.60E-02	8.74
2	90	Teflon	100	0.92	1.10	1.32	4.80E-05	5.60E-02	9.02
4	90	Teflon	18	1.09	1.35	1.56	5.20E-05	9.00E-02	9.12
5	183	Steel	51	1.64	1.34	1.78	1.40E-04	8.40E-02	8.62
6	183	Steel	56	0.71	0.36	0.68	4.20E-05	2.40E-02	8.95
9	183	Teflon	76	1.71	1.39	1.71	2.90E-04	6.20E-02	8.78
15	183	Teflon	40	1.34	1.31	1.56	1.30E-04	7.00E-02	9.11

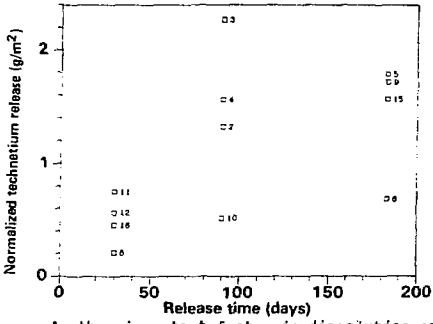

Fig. 4 Normalized technetium release as a function of time. (Sample Nos. are next to data points.)

Another important factor in dissolution rate would be the permeability of the vessel. In this experiment, the annular space of the vessel contains about 10 times as much water as the inner space; if there were free interaction of the fluids, the surface area of the glass to volume of leachant ratio (SA/V) would decrease by a factor of 10, resulting in more rapid dissolution of the glass. Figure 5 shows there was no correlation between permeability of the vessel and total release. This indicates that, with regard to the factors controlling release, the vessel is either totally permeable or totally impermeable. Since the pH was higher in the outer volume in 14 out of 16 vessels, the tuff does not appear to be totally permeable with regard to hydrogen ion.

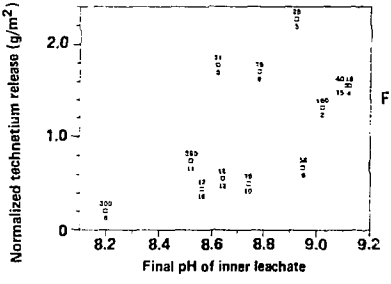

Fig. 5 Normalized technetium release as a function of final pH. (Sample Nos. are below data points; permeability constants are above data points.)

Boron, molybdenum, technetium, and neptunium were all found at constant ratios to each other within each reaction period. These relationships are illustrated in Figure 6, which shows the normalized mass loss values of neptunium as a function of the technetium normalized mass loss values. It is extremely unlikely, on the basis of previous knowledge of glass leaching, that the neptunium to technetium ratio, for example, represents differential release from the original glass matrix. It is much more likely that it is due to the elements being sequestered at varying rates in layers forming on the

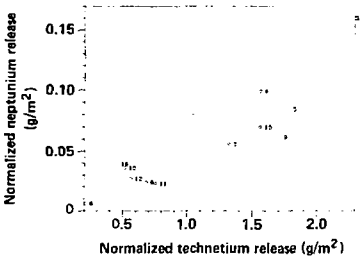

Fig. 6 Neptunium release as a function of technetium release.

glass, and in the tuff rock. The normalized release rates shown in Table VI are very low for PNL 76-68 based glasses.[6,7] This may be attributed to the relatively low pH and high silicon concentrations caused by the tuff rock surrounding the sample. The low actinide concentrations in solution are probably caused by the effects of sorption onto the rock and the pH. The rapid exchange of technetium from the inner to the outer space of the vessel indicates that it is not strongly sorbed on the rock.

CONCLUSIONS

The following conclusions are based on the data obtained in the experiment. Further details may be found in [8].

1. Boron, molybdenum, and technetium migrate through the walls of the tuff vessel. Their rate of migration appears to be controlled by the permeability of the rock as well as the length of the reaction time. The higher the permeability constant, the higher is the fraction of the leached product that is found in the annular (outer) space of the vessel. The ratios of the concentrations outside the vessel to inside are constant for all three elements within each reaction period.

2. The pH of the inner vessel leachates appears to be dependent on reaction time up to 90 days. The pH range at the end of 30 days is 8.20 to 8.64, at the end of 90 days the range is 8.74 to 9.12, and at the end of 183 days the range is 8.78 to 9.11. The tuff rock and the J-13 water appear to dominate the system since the pH of the blanks falls in the same range as the pH of the samples for each reaction period.

3. ^{237}Np, ^{238}U, and ^{239}Pu are found only in the leachates inside the tuff vessel. Both ^{237}Np and ^{239}Pu were also found in varying amounts on the surfaces of the stainless steel and Teflon supports. The residual ^{239}Pu activity is much more strongly associated with the steel than with the Teflon supports, with the Teflon supports showing a constant value, but the steel supports showing activities as much as 400 times that in solution. The ^{237}Np activity on the supports varies. No systematic retention is observed in the Teflon supports but the activity on the steel supports shows a good linear relationship with the activity in solution. The ^{237}Np in solution is 3-4 times as large as that sorbed on the steel supports.

4. Normalized elemental mass loss values were calculated for boron, molybdenum, technetium, neptunium, and plutonium. The highest normalized dissolution rate value belongs to technetium, 2.3 g glass/m^2, and the lowest values are recorded for plutonium, 10^6 times lower than the technetium value. The boron, molybdenum, technetium, and neptunium values are constant with respect to each other within each reaction period. Boron and molybdenum were released at about 85% of the technetium rate. The neptunium rates are three orders of magnitude lower and the plutonium rates about six orders of magnitude lower. The low loss rate of all elements may be attributed to the high silicon content of the leachates and to their moderate pH. Both effects appear to be caused by the large amount of tuff present in the system.

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