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The Tuff Reaction Vessel Experiment

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THE TUFF REACTION VESSEL EXPERIMENT

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 of the kind that will be used to store nuclear waste 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. Further information concerning these waste forms may be found in Oversby (1983) and references in that report.

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. This report will describe the experimental conditions and discuss the results obtained. Similar tests have been conducted (Bazan and Rego, 1985, and Bibler et al., 1984) 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.

The tuff reaction experiment used groundwater from the J-13 well at Yucca Mt. in the Nevada Test Site (Delany, 1985). The waste form consisted of glass specimens cut from ATM-8 material, which is a borosilicate glass made from a PNL 76-68 matrix. To this material low levels of technetium, neptunium, uranium, and plutonium were added to simulate a commercial high-level waste actinide composition (Oversby, 1984). It was produced and characterized by the Materials Characterization Center (MCC) at the Pacific Northwest Laboratories (PNL) (Wald, 1985).

EXPERIMENTAL

The following is a brief description of the materials and methods used to perform the entire leaching experiment. The detailed procedures are given in the Appendix.

Glass Samples

The glass specimens, prepared by MCC (Wald, 1985), were nominally 3 mm thick and 10 mm in diameter; 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. Prior to leaching, they were cleaned ultrasonically, first with deionized water and then with ethanol. This cleaning procedure is described in detail in the Appendix. The characterization of the ATM-8 glass was done by PNL (Wald, 1985) and consisted of bulk density measurements, chemical analysis, light optical and scanning electron microprobe analysis, x-ray diffraction analysis, and radiochemical analysis.

The chemical composition of the ATM-8 glass is listed in Table 1. One of the two analyses shown in this table was done at LLNL, and the other one was compiled by MCC as explained by J. W. Wald (1985). The reference composition used in all

TABLE 1.
COMPOSITION OF ATM-8 GLASS

OXIDE	MCC*(a) (wt%)	MCC STANDARD DEVIATION	LLNL(d) (wt%)
Ag2O	N.A.	--	N.A.
Al2O3	1.06	0.05	1.13
B2O3	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.
CeO2	0.11	0.03	<D.L., 0.05
Cr2O3	0.48	0.02	N.A.
Cs2O	N.A.	--	0.97 (e)
Dy2O3	0.01	0.00	N.A.
Eu2O3	<DL, 0.01	--	N.A.
Fe2O3	8.18	0.24	8.95
Gd2O3	<DL, 0.05	--	N.A.
K2O	N.A.	--	N.A.
La2O3	4.87	0.15	4.88 (e)
MgO	0.16	0.01	0.14
MnO2	0.06	0.01	N.A.
MoO3	1.98	0.04	2.24
Na2O	12.2	0.20 (b)	13.04
Nd2O3	1.66	0.06	1.55 (e)
NiO	N.A.	--	0.26
P2O5	0.57	0.07 (b)	N.A.
PdO	0.37	0.10 (c)	N.A.
Rh2O3	N.A.	--	N.A.
RuO2	0.58	0.10	N.A.
SiO2	37.8	0.70 (b)	N.A.
Sm2O3	<DL, 0.05	--	N.A.
SrO	0.47	0.01	0.50
TeO2	<DL, 0.1	--	N.A.
TiO2	2.61	0.10	2.79
Y2O3	<DL, 0.1	--	N.A.
ZnO	4.37	0.12	4.48
ZrO2	1.99	0.05	2.70
Radioactive Constituents			
NpO2	0.38	0.02 (b)	0.38 (f)
PuO2	0.11	0.11 (b)	0.097 (g)
Tc2O7	0.18	0.01 (b)	0.19 (e)
UO2	4.24	0.07 (b)	4.15
Totals	95.36		60.08

(h)
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 analysed
* PNL - 5577-8
<DL - Below the detection limit indicated

calculations in this report is that obtained at LLNL. Some of the differences in composition, as shown in Table 1, may be due to the fact that the glass material analyzed at LLNL came from a composite sample of crushed glass (bars 1, 2, 3, & 4) whereas the composition obtained at MCC came from glass samples taken from bars 7, 13, and 20 (Wald, 1985). No attempt was made at LLNL to obtain analyses from other bars to ascertain differences in composition due to inhomogeneity, particularly with respect to ^{99}Tc and the actinides. If the values for elements not analyzed at LLNL are added to the LLNL total, the result is 100.38%.

Tuff Vessels

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 crop of the Topopah Springs tuff (Knauss, 1984). The vessels were cored from large samples which did not contain large vugs or altered cracks. The ends were squared and the lid was cut using a diamond saw. The inner volume was then cored with a diamond core-barrel. The core-barrel was stopped 1 cm short of the bottom of the vessel, and the core snapped off manually. The bottom of the inside of the vesssel was then smoothed using a 240 grit diamond facing disc the same diameter as the inside of the vessel. 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 deposits (Knauss, 1984).

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 2, along with a brief description of each vessel. The procedure for measuring the permeability of each tuff vessel is given in the Appendix. Prior to starting the leaching phase of the experiment, the vessels were washed with deionized water and J-13 water according to the pre-treatment procedure outlined in the Appendix. The equilibrated J-13 water from each vessel from this procedure was saved and later used on an individual basis to perform the leaching operation. Each one of the sixteen J-13 solutions was analyzed for anions and cations and pH readings were taken. These results are shown in Table 3.

Stainless Steel and Teflon Supports

Stainless steel and 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

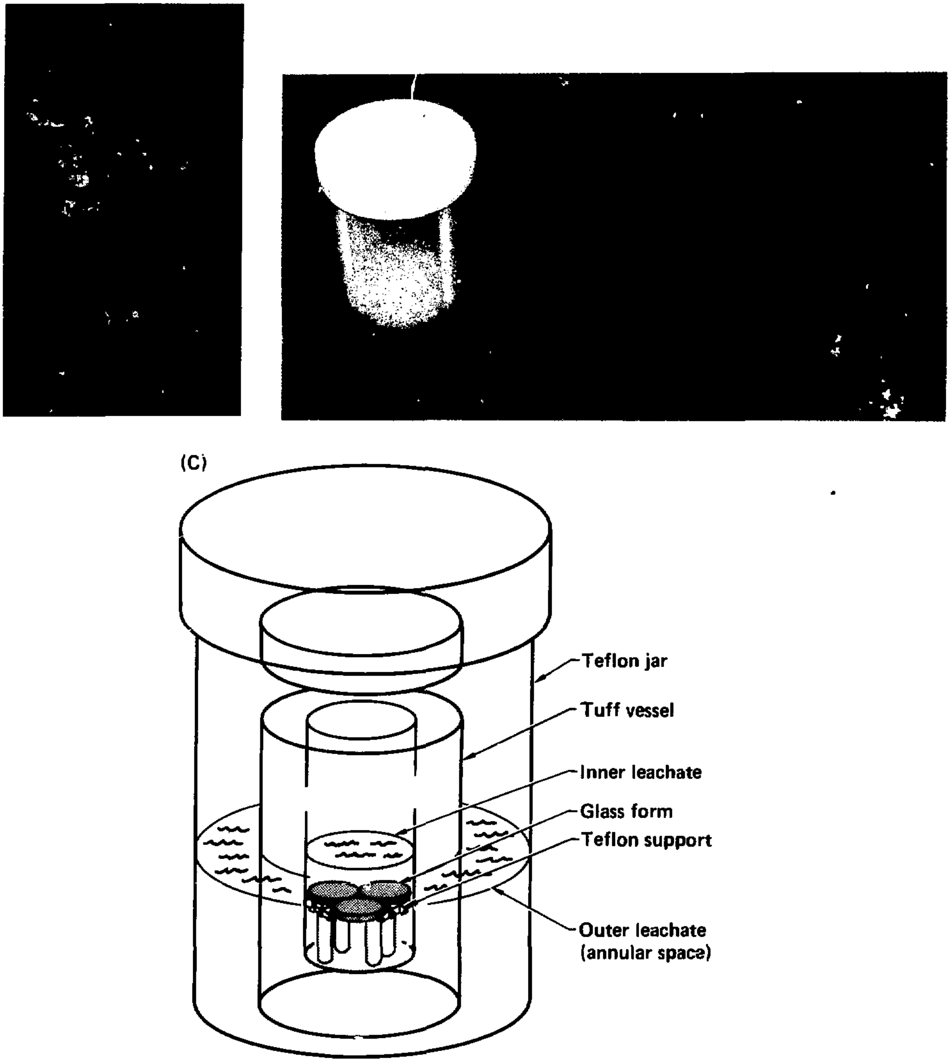

Fig. 1 (A) Tuff vessel No. 1; (B) Components of the tuff leaching test; (C) Configuration of the tuff vessel components.

TABLE 2.

VESSEL PERMEABILITY

Vessel No.	Time (d)	Permeability (ud)	Tuff Description
1	30	1900	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	590	Uniform welded tuff
12	30	12	Uniform welded tuff
7	90	1400	Large area of vapor phase alteration
3	90	26	Uniform welded tuff, one healed fracture
10	90	76	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	[illegible]	Large discolored area
15	183	40	Small discolored area

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).

Sample Configuration and Leaching Operation

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 the pre-equilibrated J-13 water, 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

TABLE 3:
TUFF VESSEL EQUILIBRATED J-13 WATER
milligrams per liter (ppm)

VESSEL/ELEM (det.lim)	Al 0.012	B 0.024	Mo 0.004	Si 0.02	Sr 0.016	Zn 0.003	Zr 0.003	Ca 0.004	K 0.82	Mg 0.001	Na 0.028	U 0.060	F 0.1	Cl 0.1	NO3 0.2	SO4 0.2
WP-11-1P	0.064	0.157	0.021	47.40	0.095	0.003	0.003	9.83	21.40	0.169	35.30	0.073	2.7	11.4	8.3	17.7
WP-11-2P	0.057	0.165	0.018	49.40	0.080	<0.003	0.003	7.06	24.30	0.111	33.40	0.097	2.4	15.9	8.3	17.5
WP-11-3P	0.054	0.161	0.017	50.60	0.068	<0.003	<0.003	6.47	28.30	0.083	32.20	0.069	2.3	9.0	8.9	19.8
WP-11-4P	0.040	0.167	0.015	54.70	0.058	<0.003	<0.003	5.02	29.70	0.026	31.80	0.086	2.5	10.5	8.4	18.0
WP-11-5P	0.055	0.186	0.014	48.10	0.068	<0.003	<0.003	9.15	23.30	0.108	33.40	<0.060	2.6	8.2	8.6	17.7
WP-11-6P	0.047	0.161	0.014	50.80	0.075	<0.003	<0.003	9.41	21.50	0.101	31.50	<0.060	2.8	9.0	9.4	17.2
WP-11-7P	0.053	0.172	0.015	61.90	0.088	<0.003	<0.003	10.50	18.60	0.099	29.50	0.065	2.5	8.7	8.4	17.2
WP-11-8P	0.041	0.152	0.018	56.20	0.075	<0.003	<0.003	8.53	20.50	0.073	31.60	<0.080	2.3	14.6	8.5	17.2
WP-11-9P	0.037	0.173	0.012	56.30	0.076	<0.003	<0.003	7.37	30.60	0.103	31.00	0.066	2.3	13.8	9.1	19.8
WP-11-10P	0.040	0.188	0.018	48.80	0.100	<0.003	<0.003	12.30	19.10	0.123	32.40	<0.060	2.5	9.8	10.8	23.9
WP-11-11P	0.031	0.150	0.014	49.80	0.071	<0.003	<0.003	8.44	21.60	0.079	31.20	<0.060	2.3	8.6	8.9	13.5
WP-11-12P	0.043	0.186	0.014	51.80	0.056	<0.003	<0.003	7.43	28.80	0.089	30.80	<0.080	2.3	7.5	8.6	17.9
WP-11-13P	0.048	0.182	0.015	49.10	0.071	<0.003	<0.003	7.67	29.80	0.118	28.80	<0.060	2.3	7.3	8.3	17.8
WP-11-14P	0.032	0.178	0.017	49.10	0.068	<0.003	<0.003	7.54	31.30	0.094	28.70	<0.060	2.2	7.5	8.5	18.1
WP-11-15P	0.035	0.172	0.014	48.70	0.088	<0.003	<0.003	7.89	27.40	0.078	33.40	<0.080	2.2	10.9	11.0	18.4
WP-11-16P	0.034	0.209	0.017	50.50	0.083	<0.003	<0.003	9.35	22.40	0.098	30.50	0.084	2.0	7.7	8.9	18.1
AVERAGE	0.044	0.170	0.016	51.43	0.075			8.44	25.00	0.095	31.72		2.4	10.0	8.9	18.5
S.D.(+/-)	0.010	0.014	0.002	3.79	0.012			1.69	4.32	0.030	1.54		0.2	2.6	0.8	1.6
%S.D.	21.63	8.52	14.00	7.37	15.78			20.04	17.28	32.21	4.85		7.4	25.8	9.0	8.8
INITIAL J-13	0.372	0.148	0.013	27.80	<0.016	0.034	N.A.	11.7	6.56	1.80	42.10	<0.080	2.3	7.2	7.0	21.5

N.A. - Not Analyzed

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. These weight data and a similar set of final weights recorded at the conclusion of each leaching interval are shown in Table 4. The step-by-step procedure including assembling and dismantling of all components of the leaching system is given in the Appendix.

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 support. The average of the inner and outer elemental concentrations of these blanks for each time interval, shown in Table 5, was used as the blank correction on the glass samples.

TABLE 4:

SOLUTION WEIGHT (VOLUME) DATA

VESSEL NO.	T(d)	PERMEABILITY CONSTANT(ud)	INITIAL INNER J-13 MASS(g)	INITIAL OUTER J-13 MASS(g)	INITIAL SUM	FINAL INNER J-13 MASS(g)	FINAL OUTER J-13 MASS(g)	FINAL SUM	WEIGHT CHANGE(g) INNER	WEIGHT CHANGE(g) OUTER	WEIGHT CHANGE SUM (%)
1	30 DAY	1900	19.77	165.53	185.30	9.81	171.20	181.01	-9.96	5.67	-2.3
8	"	300	19.79	165.52	185.31	10.57	169.90	180.47	-9.22	4.38	-2.6
16	"	12	19.76	165.65	185.41	17.73	164.40	182.13	-2.03	-1.25	-1.8
11	"	590	19.78	165.57	185.35	8.26	172.90	181.16	-11.52	7.33	-2.3
12	"	12	19.76	165.53	185.29	17.14	163.90	181.04	-2.62	-1.63	-2.3
				AVERAGE	185.3		AVERAGE	181.2		AVE	-2.3
				STND DEV	0.04		STND DEV	0.5		STND DEV	0.3
7	90 DAY	1400	19.76	165.54	185.30	18.83	158.20	177.03	-0.93	-7.34	-4.5
3	"	28	19.76	165.58	185.34	17.52	159.40	176.92	-2.24	-6.18	-4.5
10	"	78	19.77	165.50	185.27	15.03	162.50	177.53	-4.74	-3.00	-4.2
2	"	100	19.79	165.49	185.28	14.50	159.60	174.10	-5.29	-5.89	-6.0
4	"	18	19.74	165.66	185.40	14.88	157.20	172.08	-4.86	-8.46	-7.2
				AVERAGE	185.3		AVERAGE	175.5		AVERAGE	-5.3
				STND DEV	0.05		STND DEV	2.1		STND DEV	1.2
13	180 DA	1100	19.82	165.56	185.38	16.32	156.40	172.72	-3.50	-9.16	-6.8
14	"	28	19.78	165.57	185.35	18.10	153.20	171.30	-1.68	-12.37	-7.6
5	"	51	19.76	165.84	185.60	15.69	156.50	172.19	-4.07	-9.34	-7.2
6	"	56	19.77	165.57	185.34	14.25	158.30	172.55	-5.52	-7.27	-6.9
9	"	76	19.79	165.54	185.33	16.32	157.20	173.52	-3.47	-8.34	-6.4
15	"	40	19.81	165.62	185.43	14.32	157.20	171.52	-5.49	-8.42	-7.5
				AVERAGE	185.4		AVERAGE	172.3		AVERAGE	-7.1
				STND DEV	0.1		STND DEV	0.7		STND DEV	0.4

TABLE 5:

BLANK SAMPLES DATA

milligrams per liter (ppm)

SAMPLE	TIME	LEACHATE	B	Mo	Si	Na	Ca	Sr	Mg	Al	U	F	Cl	NO3	SO4
1	30	Inner	0.166	0.018	44.8	40.0	11.7	0.072	0.215	0.177	<0.06	N.A.	N.A.	N.A.	N.A.
	30	Outer	0.182	0.013	53.2	37.5	9.5	0.071	0.082	0.083	<0.06	2.2	9.7	9.3	19.0
	30	Average	0.174	0.016	49.1	38.8	10.6	0.072	0.149	0.130	-	-	-	-	-
7	90	Inner	0.262	0.013	N.A.	31.9	8.7	0.031	0.033	0.085	<0.06	N.A.	N.A.	N.A.	N.A.
	90	Outer	0.250	0.013	53.0	31.8	9.2	0.058	0.033	0.943	<0.06	2.7	9.6	8.2	18.7
	90	Average	0.256	0.013	N.A.	31.9	9.0	0.045	0.033	-	-	-	-	-	-
13	183	Inner	0.236	0.017	59.7	33.9	6.9	0.051	0.043	0.618	<0.06	2.7	8.5	9.8	20.6
	183	Outer	0.222	0.013	59.2	32.4	5.7	0.039	0.028	0.068	<0.06	2.1	7.5	9.0	18.8
14	183	Inner	0.260	0.019	63.6	39.2	8.6	0.059	0.064	0.075	<0.06	2.6	8.6	10.4	23.1
	183	Outer	0.240	0.013	62.9	32.8	5.7	0.042	0.018	0.058	<0.06	2.5	7.3	9.2	18.5
	183	Average	0.240	0.016	61.4	34.6	6.7	0.048	0.038	0.205	-	2.5	8.0	9.6	20.2

Note: N.A. - not available

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 taken with an Orion pH meter, 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. The results of the anion and cation analyses are shown in Table 6.

Portions of the inner and outer leachates were also analyzed for ^{237}Np and ^{239}Pu using an alpha pulse height spectrometer. These results are shown in Table 7. One of the analytical procedures used to measure ^{237}Np and ^{239}Pu in the leachates involved the chemical separation of neptunium and plutonium from each other and from other interfering elements such as silicon, sodium, and calcium. The radiochemical separation of the two actinides was carried out by adding ^{239}Np and ^{242}Pu tracers to the sample solutions and then separating the neptunium fraction from the plutonium fraction via a series of precipitation, ion exchange, and extraction steps (Rego, 1979). The final products, neptunium and plutonium, were electroplated on platinum discs and counted in an alpha spectrometer. This chemical procedure was used in addition to the straightforward technique of counting directly a 100 µl aliquot of the leachates for both neptunium and plutonium (Buddemeier et al., 1982).

The cesium and technetium results also shown in Table 6 were obtained using an x-ray fluorescence spectrometer and a beta proportional counter, respectively. The measurements were made on Avicel wafer samples which were prepared by pipetting a volume of solution (usually 2-3 cm^3 of the inner leachates and 50 cm^3 of the outer leachates) onto 300 mg of Avicel, a white crystalline cellulose powder, and then drying at room temperature. It took approximately 24 hours to dry the small samples and 7-8 days to dry the larger samples. The final step in this preparation procedure was to press the dried material into a 2.54-cm diameter flat wafer under 5000 psi by means of a Carver press. Both sides of the wafer were counted for the technetium analysis.

The three glass discs inside each reaction vessel were removed with a pair of tweezers, dried, weighed to determine any weight loss during the reaction time, and then stored for future surface analysis. The initial and final weights of the glass discs are given in Table 8. The stainless steel and Teflon supports were washed

TABLE 6:

ANION AND CATION ANALYSIS
milligrams per liter (ppm)

30 DAYS

INSIDE LEACHATE ANALYTICAL RESULT — NET(corrected for blank)

SPECIMEN TYPE	8 S.S.	16 S.S.	11 TEFLON	12 TEFLON	8 S.S.	16 S.S.	11 TEFLON	12 TEFLON
Al	0.53	0.24	0.65	0.28	0.40	0.11	0.52	0.15
B	0.26	0.77	0.48	0.76	0.09	0.60	0.31	0.59
Mo	0.05	0.23	0.21	0.27	0.03	0.21	0.19	0.26
Si	70.6	62.7	52.7	63.6	21.5	13.6	3.6	14.5
Sr	0.04	0.05	0.06	0.05	<0.02	<0.02	<0.02	<0.02
Zn	0.44	0.18	0.82	0.28	0.42	0.15	0.80	0.25
Zr	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01
Ca	8.04	10.20	6.74	7.16	<0.01	<0.01	<0.01	<0.01
Mg	0.06	0.14	0.15	0.10	<0.01	<0.01	<0.01	<0.01
Na	38.2	35.5	35.0	38.6	<0.03	<0.03	<0.03	<0.03
U	<0.05	N.A.	<0.05	<0.05	<0.05	N.A.	<0.05	<0.05
Tc	0.0053	0.022	0.031	0.028	0.0053	0.022	0.031	0.028
Cs	<0.2	N.A.	<0.2	<0.2	<0.2	N.A.	<0.2	<0.2
F	2.9	1.7	2.15	2.2	0.7	<0.1	<0.1	0.0
Cl	14.6	7.8	7.9	13.2	4.9	<0.1	<0.1	3.5
NO3	9.4	9.1	9.1	9.3	<0.2	<0.2	<0.2	<0.2
SO4	19.0	18.7	18.6	18.4	<0.2	<0.2	<0.2	<0.2

OUTSIDE LEACHATE ANALYTICAL RESULT — NET(corrected for blank)

SPECIMEN TYPE	8 S.S.	16 S.S.	11 TEFLON	12 TEFLON	8 S.S.	16 S.S.	11 TEFLON	12 TEFLON
Al	0.07	0.08	0.15	0.08	<0.01	<0.01	0.02	<0.01
B	0.21	0.22	0.21	0.22	0.04	0.05	0.04	0.05
Mo	0.03	0.01	0.03	0.01	0.01	<0.01	<0.01	<0.01
Si	66.6	59.3	59.5	61.6	17.5	10.2	10.4	12.5
Sr	0.06	0.05	0.05	0.04	<0.02	<0.02	<0.02	<0.02
Zn	0.04	0.02	0.07	0.01	0.01	<0.01	0.03	<0.01
Zr	0.01	<0.01	<0.01	<0.01	0.01	<0.01	<0.01	<0.01
Ca	7.10	7.50	8.04	5.76	<0.01	<0.01	<0.01	<0.01
Mg	0.03	0.04	0.03	0.03	<0.01	<0.01	<0.01	<0.01
Na	33.7	30.7	33.4	32.8	<0.03	<0.03	<0.03	<0.03
U	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05
Tc	0.00078	0.00016	0.0025	0.00018	0.00078	0.00016	0.0025	0.00018
Cs	<0.2	<0.2	<0.2	<0.2	<0.2	<0.2	<0.2	<0.2
F	3.5	2.0	2.3	2.4	1.3	<0.1	0.1	0.1
Cl	7.9	7.7	7.1	7.6	<0.1	<0.1	<0.1	<0.1
NO3	8.9	8.8	8.7	8.9	<0.2	<0.2	<0.2	<0.2
SO4	18.5	18.0	18.2	18.7	0.8	0.3	0.5	1.0

N.A. - not analyzed
S.S. - stainless steel

with 1M nitric acid for 24 hours at 90°C, and these wash-solutions were analyzed for ^{237}Np and ^{239}Pu to determine the residual actinide activity adhering to the surfaces during the leaching process. These results are also shown in Table 7.

The reaction vessels were stored for future analysis to determine the amount of the leached species deposited on the surface and pores of the tuff. This work has not been performed to date.

TABLE 6: (cont)

90 DAYS

ANION AND CATION ANALYSIS
milligrams per liter (ppm)

INSIDE LEACHATE ANALYTICAL RESULT NET(corrected for blank)

SPECIMEN TYPE	3 S.S.	10 S.S.	2 TEFLON	4 TEFLON	3 S.S.	10 S.S.	2 TEFLON	4 TEFLON
Al	0.09	0.05	0.09	0.11	<0.01	<0.01	<0.01	<0.01
B	1.45	0.70	0.79	1.13	1.19	0.44	0.52	0.87
Mo	1.02	0.23	0.45	0.74	1.01	0.22	0.43	0.73
Si	65.3	66.0	86.7	64.0	<0.02	<0.02	0.60	<0.02
Sr	0.02	0.08	0.03	0.02	<0.02	0.05	<0.02	<0.02
Zn	0.01	0.02	0.02	0.02	<0.01	<0.01	<0.01	<0.01
Zr	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01
Ca	5.26	14.10	6.71	5.01	<0.01	<0.01	<0.01	<0.01
Mg	0.05	0.07	0.04	0.03	0.02	0.04	<0.01	<0.01
Na	33.20	38.20	40.20	34.10	1.4	6.4	8.4	2.3
U	0.11(23%)	0.48(19%)	<0.05	<0.05	0.11(23%)	0.48(19%)	<0.05	<0.05
Tc	0.077	0.018	0.028	0.058	0.077	0.018	0.028	0.058
Cs	<0.2	<0.2	<0.2	<0.2	<0.2	<0.2	<0.2	<0.2
F	2.1	2.3	3.2	2.4	<0.1	<0.1	<0.1	<0.1
Cl	6.8	12.5	8.0	7.1	<0.1	2.9	<0.1	<0.1
NO3	7.2	15.4	9.2	7.9	<0.2	7.2	1.0	<0.2
SO4	15.4	28.1	20.3	16.2	<0.2	9.4	1.6	<0.2

OUTSIDE LEACHATE ANALYTICAL RESULT NET(corrected for blank)

SPECIMEN TYPE	3 S.S.	10 S.S.	2 TEFLON	4 TEFLON	3 S.S.	10 S.S.	2 TEFLON	4 TEFLON
Al	0.10	0.08	0.07	0.13	<0.01	<0.01	0.36	<0.01
B	0.33	0.29	0.33	0.32	0.07	0.02	0.07	0.06
Mo	0.05	0.03	0.05	0.04	0.03	0.01	0.04	0.03
Si	62.1	81.2	59.0	67.3	<0.02	<0.02	<0.02	<0.02
Sr	0.01	0.05	0.02	0.01	<0.01	0.02	<0.01	<0.01
Zn	0.05	0.03	0.03	0.02	0.01	<0.01	<0.01	<0.01
Zr	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01
Ca	4.57	10.40	5.10	3.98	<0.01	2.21	<0.01	<0.01
Mg	0.03	0.03	0.04	0.03	<0.01	<0.01	0.01	<0.01
Na	34.0	33.1	35.5	34.7	2.1	1.3	3.6	2.9
U	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05
Tc	0.0046	0.0013	0.0051	0.0037	0.0046	0.0013	0.0051	0.0037
Cs	<0.2	<0.2	<0.2	<0.2	<0.2	<0.2	<0.2	<0.2
F	3.0	2.4	2.9	2.5	<0.1	<0.1	<0.1	<0.1
Cl	8.3	10.8	7.4	6.2	<0.1	1.2	<0.1	<0.1
NO3	8.6	11.4	8.2	9.3	0.4	3.3	<0.2	1.2
SO4	19.0	22.4	18.0	18.5	0.3	3.7	<0.2	<0.2

N.A. - not analyzed
S.S. - stainless steel

Normalized Elemental Mass Loss

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:

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

TABLE 6:(cont)

183 DAYS

ANION AND CATION ANALYSIS
milligrams per liter (ppm)

INSIDE LEACHATE ANALYTICAL RESULT — NET(corrected for blank)

SPECIMEN TYPE	5 S.S.	6 S.S.	9 TEFLON	15 TEFLON	5 S.S.	6 S.S.	9 TEFLON	15 TEFLON
Al	0.05	0.05	0.13	0.13	<0.01	<0.01	<0.01	<0.01
B	0.79	0.50	0.72	0.71	0.55	0.26	0.48	0.47
Mo	0.51	0.20	0.43	0.52	0.49	0.18	0.41	0.50
Si	62.5	73.5	79.2	61.2	1.15	12.15	17.85	<0.01
Sr	0.04	0.04	0.06	0.05	<0.01	<0.01	0.01	<0.01
Zn	0.02	0.01	0.08	0.03	<0.01	<0.01	<0.01	<0.01
Zr	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01
Ca	9.19	6.82	7.38	6.78	2.46	0.09	0.65	0.05
Mg	0.04	0.02	0.04	0.02	<0.01	<0.01	<0.01	<0.01
Na	37.4	30.1	35.5	36.4	2.82	<0.03	0.92	1.82
U	0.06(20%)	0.04(38%)	.08(18%)	.03(36%)	0.06(20%)	.04(38%)	.08(18%)	.03(36%)
Tc	0.035	0.014	0.027	0.033	0.035	0.014	0.027	0.033
Cs	<0.2	<0.2	<0.2	<0.2	<0.2	<0.2	<0.2	<0.2
F	2.6	1.9	2.20	1.9	<0.1	<0.1	<0.1	<0.1
Cl	10.7	6.9	8.2	11.6	2.1	<0.1	<0.1	3.1
NO3	11.0	8.2	10.2	12.6	0.8	<0.2	<0.2	2.5
SO4	18.9	15.6	21.3	20.1	<0.2	<0.2	<0.2	<0.2

OUTSIDE LEACHATE ANALYTICAL RESULT — NET(corrected for blank)

SPECIMEN TYPE	5 S.S.	6 S.S.	9 TEFLON	15 TEFLON	5 S.S.	6 S.S.	9 TEFLON	15 TEFLON
Al	0.03	0.08	0.04	0.08	<0.01	<0.01	<0.01	<0.01
B	0.40	0.31	0.42	0.37	0.16	0.07	0.18	0.13
Mo	0.07	0.03	0.08	0.07	0.05	0.01	0.06	0.05
Si	57.4	60.0	73.8	65.3	<0.02	<0.02	12.45	3.95
Sr	0.04	0.03	0.04	0.04	<0.01	<0.01	<0.01	<0.01
Zn	0.00	0.01	0.01	0.01	<0.01	<0.01	<0.01	<0.01
Zr	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01
Ca	6.57	4.99	4.95	5.57	<0.01	<0.01	<0.01	<0.01
Mg	0.03	0.03	0.02	0.02	<0.01	<0.01	<0.01	<0.01
Na	30.2	26.2	29.2	36.6	<0.03	<0.03	<0.03	2.02
U	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05
Tc	0.0071	0.0028	0.0073	0.0061	0.0071	0.0028	0.0073	0.0061
Cs	<0.2	<0.2	<0.2	<0.2	<0.2	<0.2	<0.2	<0.2
F	2.30	2.1	2.5	2.6	<0.2	<0.2	0.2	0.3
Cl	9.0	6.8	7.3	11.5	1.6	<0.1	<0.1	4.1
NO3	9.4	7.1	9.0	13.0	0.3	<0.2	<0.2	3.9
SO4	16.1	13.3	16.9	19.7	<0.2	<0.2	<0.2	1.0

N.A. - not analyzed
S.S. - stainless steel

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 concentration of element x in the leach solution was obtained by adding the concentration inside the tuff vessel to the concentration in the annular space using the formula:

$$\left[(C_x)(V)\right]_{\text{Total}} = \left[(C_x)(V)\right]_{\substack{\text{Inner}\\\text{Leachate}}} + \left[(C_x)(V)\right]_{\substack{\text{Outer}\\\text{Leachate}}} \qquad (2)$$

TABLE 7:

NEPTUNIUM-237 and PLUTONIUM-239 DATA

Sample	Time	Support	Inner Leachate dpm Np-237	Inner Leachate dpm Pu-239	Outer Leachate dpm/0.1cm3 Np-237	Outer Leachate dpm/0.1cm3 Pu-239	Supports dpm Np-237	Supports dpm Pu-239
8	30	S.Steel	23 +/- 6%	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	67 +/- 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 +/- 1%	4 +/- 16%	<0.1	<0.02	19	203
4	90	Teflon	366 +/- 5%	5 +/- 12%	<0.1	<0.02	21	409
5	183	S.Steel	330 +/- 1%	12 +/- 6%	<0.1	<0.02	108	4920
6	183	S.Steel	96 +/-2%	4 +/- 10%	<0.1	<0.02	20	2790
9	183	Teflon	245 +/- 2%	27 +/- 5%	<0.1	<0.02	11	295
15	183	Teflon	273 +/- 1%	9 +/- 6%	<0.1	<0.02	28	361

Note: Radiochemical Method Inner Sample 5: Np=353 dpm (1%), Pu=9 dpm (13%)
Radiochemical Method Inner Sample 15: Np=302 dpm (1%), Pu=7 dpm (12%)
Radiochemical Method Outer Samples 5,6,9,15: Np=<0.1, Pu=<0.02 dpm

TABLE 8.

GLASS SAMPLE WEIGHT DATA

SAMPLE No.	REACTION TIME (d)	Sample Weights Initial (g)	Sample Weights Final (g)	Weight Loss (g)
8	30	2.1737	2.1700	0.0037
16	30	2.1401	2.1399	0.0002
11	30	2.1228	2.1226	0.0002
12	30	2.1377	2.1243	0.0134
3	90	2.2410	2.2403	0.0007
10	90	2.1874	2.1878	0.0004
2	90	2.1697	2.1694	0.0003
4	90	2.1852	2.1835	0.0017
5	183	2.1453	2.1434	0.0019
6	183	2.2498	2.2487	0.0011
9	183	2.2038	2.2030	0.0008
15	183	2.1420	2.1416	0.0004

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

$$NL_i = \frac{(a_x)(V)}{(a_o)(SA)}(W_o) \qquad (3)$$

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 2 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. The altered and discolored regions correspond to vapor phase alteration areas formed when the tuff was cooling after emplacement (Knauss, 1984). 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.

The permeability constants of the four blanks, vessels Nos. 1, 7, 13, and 14 were 1900, 1400, 1100, and 28 μd respectively. Vessel 1 was run with the 30-day samples, vessel 7 was run with the 90-day samples, and vessels 13 and 14 were run with the

183-day samples. The first three permeability constants are the highest in the set of sixteen vessels and the fourth is representative of the lower end.

There seems to be some evidence that porosity affects changes in volume inside and outside the vessel, at least during the first 30 days. There is an apparent loss of weight in the inner leachate of sample No. 1; only 9.8 g were recovered from the initial 19.77 g, whereas an increase in weight from 165.5 g to 171.2 g was recorded in the outer leachate. All three 30-day samples (1,8,11) with high porosities show this pattern. In comparison, the weight changes for sample 7, the 90-day blank with a permeability constant of 1400 µd, show a 0.93 g loss in the inner leachate and a 7.34 g loss in the outer leachate. The 183-day blanks, samples 13 and 14, with permeability constants of 1100 and 28 µd respectively, are very much like sample 7 in behavior. It should be pointed out also that transport from the inner to the outer spaces of the vessel took place in the absence of a significant hydraulic gradient since the inner and the outer levels were set to the same height initially.

These results indicate that the tuff vessels may vary widely in terms of the degree to which exchange can occur between the water inside the vessel and the water surrounding it. Because of the localized differences in permeability, interactions of the leached waste products with the surface and interior of the vessels can be expected to be very non-uniform. In future work of this type, all vessels should undergo a careful permeability measurement and leak-mapping process which will permit selection and matching of vessels having equal permeability characteristics. The measured characteristics should be helpful in interpreting the final results, such as the amount of leachate exchange with the external water. Identification of the high porosity/permeability mineral phases and the specific zones of leakage can also help in the study of surface sorption or precipitation, and penetration of the leached waste products into the rock. In this study, the vessels of highest permeability were used as blanks.

Shown in Table 4 are the weight data for the solutions inside and outside the vessel at the beginning (initial weight) and at the end (final weight) of the experiment. The combined weights of the inner and outer leachates indicate that evaporation losses and/or uptake of the liquid by the rock is quite uniform in each of the three groups of samples despite the permeability differences from vessel to vessel. It appears, that the overall change in weight as shown in the last column of Table 4 is time dependent. The average losses from the entire system are 2.3%, 5.3%, and 7.1% for the 30-day, the 90-day, and the 183-day samples, respectively.

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 results of the elemental analysis are summarized in Table 5. The inner and outer leachate concentrations were averaged as shown in the table 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 9 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 two-week equilibration procedure of the vessels prior to the leaching phase. The average pH value of the 16 solutions listed in Table 9 is 8.48 ± 0.18, which is slightly lower than the pH values of the leachates at the end of each leaching period.

TABLE 9.

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	8.44	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 (Oversby, 1984), 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 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 (Mendel, 1984). The lower pH values in this

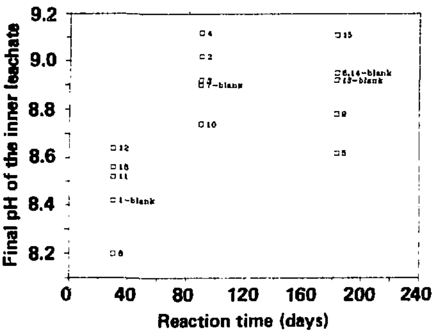

Fig. 2. pH of the leachate inside the tuff vessel as a function of reaction time. (Sample Nos. are next to data points.)

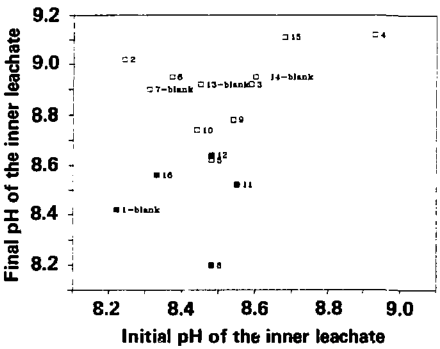

Fig. 3. Final pH inside the tuff vessel as a function of initial pH. (Sample Nos. are next to data points. Dark data points are 30-day samples.)

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.

Boron

The boron concentrations in ppm were obtained by ICP analysis and are shown in Table 10. In the 30-day samples, the concentrations range from 0.09 to 0.60 ppm in

TABLE 10

B, Mo, Tc FRACTIONS IN ANNULAR SPACE

					BORON			MOLYBDENUM			TECHNETIUM		
VESSEL NO.	PERM (ud)	REACTION TIME(d)	FINAL WEIGHT(g) INNER	OUTER	PPM Inner	Outer	Fraction	PPM Inner	Outer	Fraction	PPM Inner	Outer	Fraction
8	300	30	10.57	169.9	0.09	0.04	0.88	0.03	0.01	0.84	0.0053	0.00078	0.70
16	12	30	17.73	164.4	0.60	0.05	0.44	0.21	-0.01		0.022	0.00016	0.06
11	590	30	8.28	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	0.45	0.28	-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	[illegible]	90	16.03	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	0.43	0.04	0.51	0.028	0.0051	0.66
4	18	90	14.88	157.2	0.87	0.06	0.42	0.73	0.03	0.30	0.058	0.0037	0.40
5	61	183	15.69	156.5	0.55	0.16	0.74	0.49	0.05	0.51	0.035	0.0071	0.67
6	56	183	14.25	158.3	0.28	0.07	0.75	0.18	0.01	0.38	0.014	0.0028	0.68
9	78	183	16.32	157.2	0.48	0.18	[illegible]	0.41	0.08	0.58	0.027	0.0073	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

the inner leachates and from 0.04 to 0.05 ppm in the outer leachates. Using these data and the volumes of the leachates, the calculated fractions of boron in solution found in the annular space are 88, 44, 73, and 45% for the four samples with permeabilities of 300, 12, 590, and 12 µd respectively. The apparent rather high percentage of boron in the annular space for the higher permeability samples implies a faster leakthrough from the inside to the outside of the vessels. This suggestion is further corroborated by the faster loss of solution from the inside; the weight-loss data in Table 4 indicate that the original solutions have been reduced nearly in half at the end of 30 days.

In the 90-day samples, the boron concentrations range from 0.44 to 1.19 ppm in the inner leachates and from 0.02 to 0.07 ppm in the outer leachates. The permeability constants in this group range from 18 to 100 µd. As in the previous case, the sample with the highest concentration of boron in the annular space (60%) corresponds to the vessel with the highest permeability constant (100 µd).
In the 183-day samples, the boron concentrations range from 0.26 to 0.55 ppm in the inner leachates and from 0.07 to 0.18 ppm in the outer leachates. The calculated fractions in the annular space of the total boron in solution for the four samples are very uniform: 74, 75, 78, and 75%. Likewise, the permeability constants of the four vessels are very similar: 51, 56, 76, and 40 µd, respectively.

Technetium

The measured technetium concentrations in ppm are shown in Table 10. These results, along with the volumes of the leachates, were then used to calculate (a) the total concentrations inside and outside the vessel, and (b) the fraction of the dissolved technetium in the annular (outer) space. The technetium ratios for the 30-day samples are clearly dependent on the permeability constant of the vessels. Samples 8 and 11, with permeabilities of 300 and 590 µd, exhibit technetium concentrations of 70 and 63% in the annular space as opposed to only 6% for samples 12 and 16, which have permeabilities of 12 µd.

In the 90-day samples, the technetium concentrations in the annular space do not vary as greatly but neither do the permeabilities of the vessels. The concentrations range from 35 to 66% and the permeabilities range from 18 to 100 µd.

In the 183-day samples, the gap is even narrower for both the technetium concentrations in the annular space (67 to 72%) as well as the permeability constants (40 to 76 μd).

Molybdenum

The molybdenum results are shown in Table 10. Using the concentrations, ppm, and the volume-data for the inner and outer leachates, fractions of the leached molybdenum in the annular space were calculated.

The analysis of the inner leachates was sufficiently reliable so that the amounts measured in all of the samples were comfortably in excess of the blank correction. On the other hand, in the outer leachates, the molybdenum concentrations in the four 30-day samples are almost identical to the molybdenum concentration in the blank sample. In fact, samples 16 and 12 are on the negative side after the blank correction is applied, and samples 8 and 11 are barely on the positive side. Despite these difficulties in sensitivity, the calculated molybdenum fractions in the annular space for samples 8 and 11 at 84 and 52%, respectively, are in close agreement with the boron and technetium results.

The molybdenum concentrations in the outer leachates of the 90-day samples are slightly larger than in the 30-day samples except for sample 10, which exhibits a molybdenum concentration of 0.01 ppm; the other three samples show 0.03, 0.04, and 0.03 ppm. The calculated molybdenum fractions in the annular space are 21, 33, 51, and 30%, which are also in reasonable agreement with the boron and technetium results.

In the 183-day samples, the molybdenum fractions in the annular space are 51,38, 58, and 52%. These results are generally lower than those obtained for boron and technetium, as shown in Table 10.

Uranium

Uranium analysis was performed on both the inner and the outer leachates by two methods, ICP and x-ray fluorescence. The ICP results were all below the limit of detection of the instrument, which is 0.05 ppm. The x-ray fluorescence measurements were made on the same samples used for the cesium and the technetium analyses. Since the sample size in the XRF technique was increased to 2-3 cm^3 for the inner leachates and to 50 cm^3 for the outer leachates compared to 1 cm^3 taken for ICP, the sensitivity for uranium was thus increased correspondingly. Nevertheless, the uranium concentrations in the outer leachates are still non-detectable, as shown in Table 6.

In the 30-day inner leachates, the concentrations are also non-detectable, but in the 90-day inner leachates the uranium concentrations are 0.08, 0.48, <0.05, and 0.05 ppm. In the 183-day inner leachates, the concentrations are 0.06, 0.04, 0.08, and 0.03 ppm. All of these values, as shown in Table 6, have 20-40% uncertainties, due to counting.

Cesium

The cesium analysis of the leachates was performed using x-ray fluorescence. The samples used for counting were the same samples prepared for the uranium x-ray fluorescence analysis described above. The results in Table 6 are expressed as <0.2 ppm, indicating that the cesium concentration in the samples is below the limit of detection of the counting system. However, the cesium concentrations in both the inner and outer leachates would have been detectable if cesium was released from the glass, and into solution, at the same rate as boron, molybdenum, or technetium. This maximum cesium release was calculated on the basis of the boron normalized mass loss values shown in Table 11 and the boron fractions found in the inner and outer leachates (Table 10). The results of these calculations confirm that cesium should be detectable in the samples prepared for analysis using the x-ray fluorescence technique. Since the actual measurements performed on those samples indicate that the cesium concentrations are <0.2 ppm, one is led to believe that the cesium is deposited on the surfaces of the glass or the tuff vessel.

Plutonium

^{239}Pu was quantified in both the inner and outer leachates as well as in the stainless steel and Teflon supports. These data are shown in Table 7. The total ^{239}Pu activity in the inner leachates ranges from 1 to 27 dpm. In the outer leachates, the concentrations are below the limits of detection of the counting system (<0.02 dpm). An extra effort was made to quantify the ^{239}Pu activity in the 183-day outer leachates by processing 10 cm^3 of the sample solutions through a plutonium-neptunium radiochemical separation and then counting the separated plutonium fraction. The normal procedure is to directly count a 100 µℓ sample and then calculate the plutonium and neptunium concentrations from the alpha pulse height spectrum. The results obtained from both of these methods indicate that plutonium does not move through the rock.

As mentioned above, the stainless steel and Teflon supports were also analyzed for ^{239}Pu. The supports were heated with 1M nitric acid for 24 hours at 90°C and the resulting solutions were counted in the same manner as the 100 μℓ samples. The ^{239}Pu activity in these "wash" solutions was significantly larger than in the leachates; the range of the concentrations is from 198 dpm at the end of the 30-day reaction time to 4900 dpm at the end of the 183-day reaction time. 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. The residual ^{239}Pu activity appears to be much more strongly associated with the stainless steel supports than with the Teflon supports (Figure 4), with the Teflon supports showing a constant value but the steel supports showing activities approximately 400 times that in solution.

Neptunium

The inner and outer leachates including the blank samples were analyzed for ^{237}Np. Additionally, the stainless steel and Teflon supports were analyzed for ^{237}Np. These data are shown in Table 7. The ^{237}Np activity in the inner leachates ranges from 23 to 90 dpm at the end of 30 days, from 140 to 623 dpm at the end of 90 days, and from 96 to 330 dpm at the end of 183 days. Two of the 183-day samples were analyzed by separating radiochemically the neptunium fraction from the plutonium using 1 cm^3 of the sample solutions. The normal procedure is to evaporate 100 μℓ directly onto a platinum disc and count for both neptunium and plutonium. The results of the two methods are shown in Table 7. The ^{237}Np activity in the outer leachates was below the limit of detection of the counting system (<0.1 dpm). The four 183-day outer leachates were also analyzed by the alternate method of taking 10 cm^3 of the solutions and separating the neptunium fraction from plutonium as mentioned above. The results of these analyses confirm the results obtained by the normal method, as shown in Table 7. The residual ^{237}Np activity on the steel and Teflon supports varies greatly from sample to sample. The amount sorbed on the Teflon supports is small and not systematic. The activity on the steel supports shows a good linear relationship with the activity in solution (Figure 5). There is approximately 3-4 times as much ^{237}Np in solution as is sorbed on the steel supports.

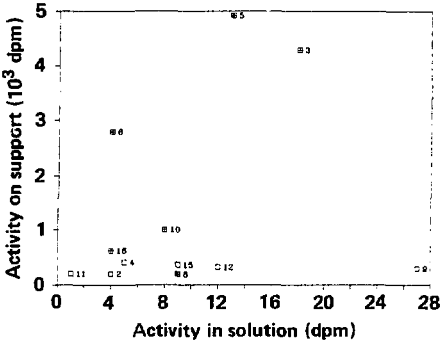

Fig. 4. Plutonium activity on the stainless steel and Teflon supports as a function of activity in solution. (Sample Nos. are next to data points. Crossed data points are stainless steel and empty data points are Teflon.)

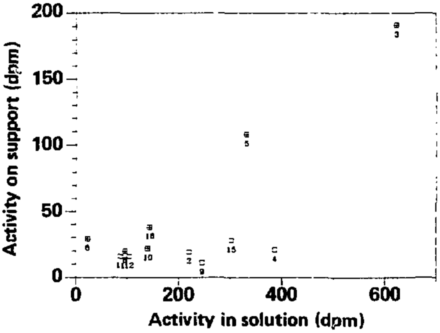

Fig. 5. Neptunium activity on the stainless steel and Teflon supports as a function of activity in solution. (Sample Nos. are below data points. Crossed data points are stainless steel. Empty data points are Teflon.)

Normalized Elemental Mass Loss

Normalized elemental mass loss values were calculated for boron, molybdenum, technetium, neptunium, and plutonium. These are shown in Table 11. The boron, molybdenum, and technetium values were calculated using the sum of the inner and outer leachate concentrations; 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 6, the trend is that of initial rapid release followed by slower release. This trend has been observed previously in static leach testing (e.g., Bazan & Rego, 1985). 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 (Mendel, 1984). In this system, the pH

TABLE 11

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	8.84
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	9.90E-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

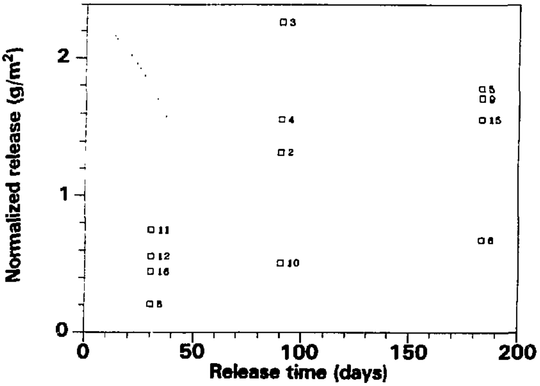

Fig. 6. Normalized technetium release as a function of time. (Sample Nos. are next to data points.)

appears to be controlled by the tuff vessel, yet the glass release is still strongly correlated to the pH (Figure 7).

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 and complete dissolution of the glass. Figures 7 and 8 show that there is 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.

Another factor expected to be strongly correlated to both pH and release is the total silicon concentration in the leachates. In this case, however, no correlation is apparent.

The elements boron, molybdenum, technetium, and neptunium were all found at constant ratios to each other within each reaction period. These relationships are illustrated in Figures 9, 10, and 11 which are plots of the normalized mass loss values of boron, molybdenum, and neptunium as a function of the technetium normalized mass loss values. This linear relationship may even hold for the ^{239}Pu data, Figure 12, even though ^{239}Pu was found at very low levels in solution. It is extremely unlikely, on the basis of previous knowledge of glass leaching, that these

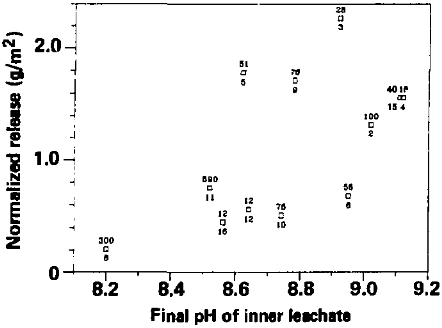

Fig. 7 Normalized technetium release as a function of final pH. (Sample Nos. are below data points; permeability constants are above data points.)

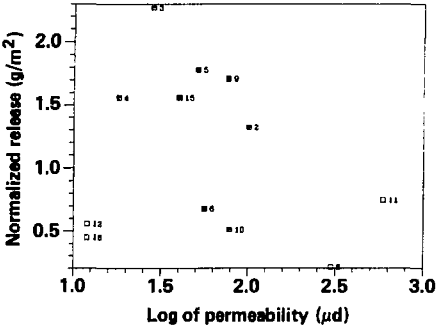

Fig. 8. Correlation between normalized technetium release and vessel permeability. (Sample Nos. are next to data points.)

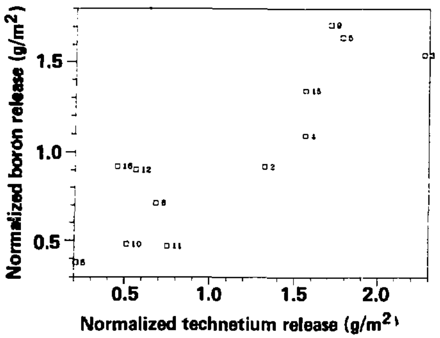

Fig. 9. Boron release as a function of technetium release. (Sample Nos. are next to data points.)

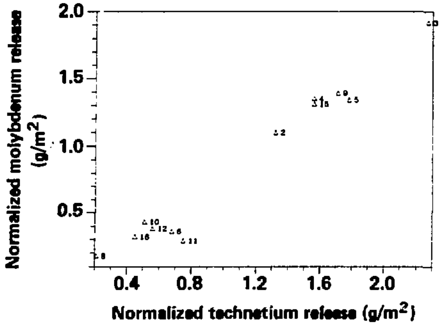

Fig. 10. Molybdenum release as a function of technetium release.

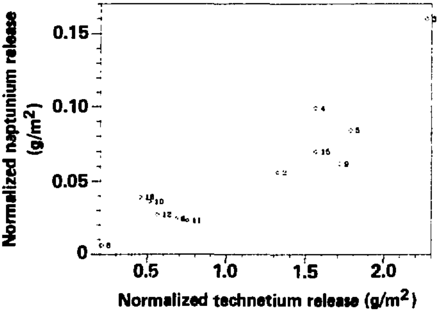

Fig. 11. Neptunium release as a function of technetium release.

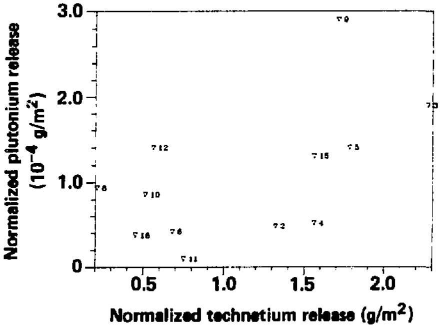

Fig. 12. Plutonium release as a function of technetium release.

ratios represent differential release from the original glass matrix. It is much more likely that they are due to the elements being sequestered at varying rates in layers forming on the glass, and in the tuff rock. The normalized release rates shown in Table 11 are very low for PNL 76-68 based glasses (Mendel, 1984; McVay and Robinson, 1984). 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.

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. 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 greatly from sample to sample. 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. It should be noted that both the neptunium and plutonium mass loss values are calculated from the concentrations in solution only. The boron, molybdenum, technetium, and

neptunium values are constant with respect to each other within each reaction period. The average technetium normalized mass loss values are 0.5 g/m^2 at the end of 30 days, 1.4 g/m^2 at the end of 90 days, and 1.4 g/m^2 at the end of 183 days. 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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APPENDIX

Procedure No. 1

CLEANING, MEASURING, AND WEIGHING OF THE GLASS DISCS

The following procedure was used with the ATM-8 glass discs upon receipt from MCC and, prior to starting the leaching phase of the experiment. The initial handling of the already-cut specimens was performed inside a glove box because of the alpha activity contained in the glass and the packaging materials. The steps described below were subsequently performed outside the glove box but still with extreme care.

1. Clean the entire group of 36 discs in an ultrasonic bath, first with deionized water for five minutes and then with ethanol three times for five minutes each.

2. Rinse with deionized water thoroughly to wash away the ethanol and accumulated organics.

3. Place the discs in an oven at 100°C and dry to constant weight.

4. Measure the dimensions (thickness and diameter) of each disc using a micrometer. Calculate the surface area and record in a notebook.

5. Separate the discs in groups of three and weigh accurately to ±0.1 mg using an analytical balance. Record the weight and assign each group of three discs to a vessel properly identified.

Procedure No. 2

PERMEABILITY MEASUREMENTS

Permeability measurements of tuff vessels are necessary because differences in permeability can lead to major differences in exchange of water between the interior and exterior parts of the rock vessel. Also, the penetration of the leached products into the rock will be spatially variable. Therefore, characterization of each tuff vessel prior to leaching is recommended in order to facilitate interpretation of the chemical data and the targeting of specific rock surface sites for subsequent analysis.

In this experiment, all sixteen vessels were subjected to the following procedure:

1. Assemble a constant-head permeameter consisting of a buret inserted into a one-hole rubber stopper which makes a tight fit with the opening of the rock vessel.

2. Fill the vessel with deionized water and allow to sit for 24 hours prior to the permeability measurements. This step permits the rock to become saturated.

3. Fill the vessel and buret with water and fit the stopper into the vessel.

4. Record the time required for 1 cm^3 of water to leak out of the vessel; refill the buret and repeat the measurement until consistent readings are obtained.

5. Calculate the permeability constant (K) from the formula $K = Q \times L/A \times H$, where Q is the flow rate (cm^3/min), L is the wall thickness of the vessel (cm), A is the vessel interior surface area (cm^2), and H is the head (cm) taken as the distance from the midpoint of the vessel interior to the top of the initial buret water column. The permeability constant (K) is expressed in microdarcy (μd) units.

Procedure No. 3

CONDITIONING OF VESSELS AND EQUILIBRATION OF J-13 WATER

All tuff reaction vessels which were used in this experiment were pre-treated by the following procedure. In all cases, the reaction vessel and lid were totally submerged.

1. Soak overnight in deionized water (DIW). Take sample of supernatant liquid for anion analysis, and discard the remainder.

2. Add new DIW. Heat at 90°C for 24 hours. Remove water, taking a sample of water for both cation and anion analysis.

3. Repeat step 2 an additional two times with new water each time.

4. If anion analysis shows essential absence of anion release, proceed with pre-equilibration step. If substantial anion concentrations are detected, repeat step 2 until release is no longer detected. (In this experiment, step 2 was repeated three times. The concentrations of F, Cl, NO_3, and SO_4 anions in the 16 samples at the end of the third cycle ranged from 0.1 to 0.2 ppm for F, 0.4 to 1.0 ppm for Cl, 0.3 to 2.0 ppm for NO_3, and 0.2 to 1.0 ppm for SO_4.)

Equilibration Step:

Once all caliche has been removed, arrange reaction vessel in the outer container and add J-13 water to outside and inside of vessel. Place lid on vessel and place lid on outer container. Heat in 90°C oven for two weeks to pre-equilibrate water. Cool to room temperature, and remove water to a clean container. Take a sample of water for ICP and anion analyses. Assemble test apparatus as described in test protocol. Start test.

Procedure No. 4

ASSEMBLING AND DISMANTLING PROCEDURE

The following procedure was used to assemble the leaching package at the beginning of the experiment and to dismantle the components at the end of each leaching interval. This procedure begins immediately after the pre-treatment of the tuff vessel and equilibration of the J-13 water.

1. Place the stainless steel or Teflon support at the bottom of each tuff vessel.

2. Place the waste form (three glass discs in this experiment) flat on the support and add the required amount of J-13 water to the interior of the vessel. This amount (approximately 17 cm^3) is sufficient to cover the glass discs totally and should yield a surface area to volume ratio of 0.39 cm^{-1}. The weight of the J-13 water is to be recorded as the initial weight of the inner leachate.

3. Cover the vessel with its loose cap and place inside a 500 cm^3 Teflon jar. Carefully add a known amount of the equilibrated J-13 water to the annular space between the vessel and the jar. This amount (approximately 160 cm^3) should reach the same height as the water inside the vessel.

4. Screw-cap the Teflon jar tightly and weigh the entire package to record the gross starting weight. This step is very important because it will serve to determine loss due to evaporation when compared to the final gross weight.

5. Cautiously place each Teflon jar inside a Blue M oven where the temperature is 90 ± 1°C. This temperature should be closely monitored throughout the experiment by means of an Omega OM-202 Temperature Logger.

6. Twice during the first 24 hours remove the Teflon jar and carefully tighten its screw-cap. This precaution is necessary to minimize losses due to evaporation.

7. At the conclusion of each leaching interval (30, 90, and 183 days), remove the Teflon jar from the oven and let it cool to room temperature. Weigh and record the final gross weight.

8. Open the jar and carefully remove the capped vessel with a pair of large forceps. Set the lid aside and transfer the inner leachate to a 25 cm^3 Teflon capsule by means of a plastic syringe through a 45 µm millipore filter.

9. Record the weight of the solution. This portion is now known as the inner leachate.

10. Weigh the Teflon jar containing the outer leachate and record this weight as final. This portion will be larger than at the beginning of the experiment if there is a contribution from the inner leachate or smaller if there is evaporation out of the Teflon jar. Transfer the outer leachate to a clean Teflon container by means of a plastic syringe through a 45 µm millipore filter.

11. Remove 1 cm^3 aliquots from each of the two leachates for anion analysis.

12. Take the pH of the two leachates with a pH meter that has 0.01 units sensitivity.

13. Acidify the remaining portions with nitric acid so that the final acid concentration is 2% by volume. Close the capsules and place in a 90°C oven overnight.

14. At the end of this period, remove the capsules from the oven and let cool to room temperature.

15. From each solution, remove appropriate aliquots for ICP, alpha spectrometry, and x-ray fluorescence analyses.