

LEACH TESTING IN SIMULATED REPOSITORY GROUND WATERS

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ABSTRACT

Two experimental waste forms developed at the Idaho National Engineering Laboratory, a borosilicate glass and a fused glass-ceramic, iron-enriched basalt, were leach tested at temperatures from 30°C to 250°C and in a gamma field of $\sim 10^4$ Gy/h at $\sim 40^\circ\text{C}$. Leachants used were aerated and air-free distilled water, a saturated salt brine, a simulated CO_2 containing anoxic ground water, and anoxic water equilibrated with basalt and in contact with ground basalt. The specimens were spiked with tracers to simplify leachate analysis. The gamma field increased leaching about seven fold in aerated water and about two fold in the other leachants. Usually little more material was leached in 130 days than in 28 or 65 days. The lowest leach rates were found in water in contact with ground basalt, and a good fraction of the activity was adsorbed on the solid basalt. Both waste forms were about equally leach resistant except for cobalt which was only one seventh as leachable from the ceramic as from the glass. A few Soxhlet leach tests and some tests in 1M CH_3COOH -0.1M CH_3COONa were also run.

INTRODUCTION

Two potential waste forms have been studied at the Idaho National Engineering Laboratory (INEL), a glass waste forms for immobilizing calcined high-level waste¹ and a durable fused ceramic, iron-enriched basalt (IEB)² for immobilizing transuranic waste stored at the INEL. The IEB also shows promise for immobilizing high-level reprocessing waste. The waste forms have been extensively leach tested in distilled water and a few tests were made in saturated salt brine.³⁻⁵ Some leach tests have also been run in a gamma radiation field of $\sim 10^4$ Gy/h at the ambient temperature of the gamma facility, $\sim 30^\circ\text{C}$.⁶ These tests showed about a seven-fold increase in leaching in distilled water in contact with air and about a two-fold increase in salt brine.

Since the major cause for increased leaching in the gamma irradiated water appears to be radiolytic nitric acid,⁷⁻¹⁰ and since the enhancement of leaching was much less in salt brine,⁶ additional leach tests were run in a gamma field using boiled air-free distilled water, a simulated granitic ground water containing Fe^{3+} and CO_2 ,¹¹ and air-free water equilibrated with Snake River Plain basalt plus solid ground basalt, all protected from the air by an argon blanket. The tests were again run at the ambient temperature of the gamma facility, now $\sim 40^\circ\text{C}$, and comparison tests were run at the same temperature in the absence of the field. The CO_2 containing leachant was interesting since radiolysis of CO_2 in water can form organic acids, e.g. HCOOH and $\text{H}_2\text{C}_2\text{O}_4$,^{12,13} which can enhance leaching.

In addition, leach tests were run (in the absence of the gamma field) in distilled water, in the salt brine, and in the two simulated ground waters at 90°C, 170°C, and 250°C in order to determine the effect of temperature on leaching. A few Soxhlet tests and some tests in pH 3.8 acetic acid-sodium acetate buffer were also run to compare the leaching of the present samples with samples previously tested.^{3,14}

PREPARATION OF SAMPLES

The samples were prepared in the same manner as for the previous gamma field leach tests.⁶ The glass was prepared from simulated ICPP calcined waste, see Table I.¹⁵ The fused ceramic, IEB, was prepared from simulated commercial high-level reprocessing waste, see Table I.¹⁶⁻¹⁸ Both waste forms were spiked with $\sim 10^4$ Bq/g each of 2.6y ^{22}Na , 5.26y ^{60}Co , 64d ^{95}Zr + 35d

TABLE I

Composition of Waste Forms, Weight %

	IEB	Glass
Frit	80	66.7
SiO_2	39.9	46.9
B_2O_3	----	5.7
Na_2O	5.2	8.5
Li_2O	----	4.1
CuO	----	1.4
Al_2O_3	7.8	----
Fe_2O_3	11.8	----
FeO	3.4	----
TiO_2	0.23	----
CaO	6.7	----
MgO	2.9	----
K_2O	1.9	----
P_2O_5	0.09	----
SO_3	0.01	----
Simulated Waste	20	33.3
Fissium ^{3,6}	12.0	0.67
Al_2O_3	2.0	4.5
$\text{K}_2\text{Cr}_2\text{O}_7$	0.2	0.10
Fe_2O_3	2.0	0.47
MgO	0.8	0.60
Na_3PO_4	2.0	0.07
NiO	0.2	0.07
CaF_2	----	13.0
ZrO_2	----	7.0
UO_2	----	0.03
ThO_2	----	0.03
CaCO_3	----	5.4
NaNO_3	----	0.77
B_2O_3	----	0.67

^{95}Nb daughter, 10.6y ^{133}Ba , 30.2y ^{137}Cs , 284d ^{144}Ce and 432y ^{241}Am . The glass ingredients were melted at 1100°C in alumina crucibles, and the melt poured on a graphite block and annealed. The IEB ingredients were melted at 1500°C in alumina crucibles, then cooled to 1000°C and held at that temperature overnight, and finally slowly cooled to room temperature. The IEB contained crystalline spinel (magnetite) and augite, $(\text{Ca},\text{Fe},\text{Mg})(\text{Si},\text{Al})\text{O}_3$, plus 30-50% aluminosilicate glass.^{4,19}

TABLE II
Simulated Ground Water Leachants,
Concentration, MMol/Liter

	WIPP Brine B	Reducing Carbonate Water	Water Equil- ibrated With Basalt
Na ⁺	5015	1.82	0.035
Ca ⁺⁺	20	0.50	0.072
Mg ⁺⁺	0.4	0.25	0.0066
Fe ⁺⁺	----	0.25	0.0007
Al ³⁺	----	----	0.052
Cl ⁻	4996	0.82	-----
SO ₄ ⁼	27	1.0	-----
Br ⁻	5	----	-----
HCO ₃ ⁻	----	1.0	-----
SiO ₂	----	0.25	0.46
CO ₂	----	0.3	-----
pH	6.5	6.9	7.0

Leach specimens with an area of 2-4 cm² were diamond sawed from the solidified melts. The saw gave a 400-600 grit finish. Before leaching, the areas were determined, the specimens cleaned in water and ethanol in a ultrasonic bath, and then dried and weighed on a microbalance. The tracer content of the specimens was determined by counting the entire piece at a 9-cm distance with a standardized Ge(Li) gamma spectrometer.

LEACH TESTING

Most of the leach tests were patterned after the Materials Characterization Center's MCC-1 static leach test,²⁰ with modifications necessary because of the high radiation field. Some long-term tests followed the International Atomic Energy Agency standard test²¹ where the leachant was changed at intervals. The leachants used were distilled water in contact with air, distilled water boiled in Pyrex glass and cooled under argon to keep it air free, a saturated salt brine (essentially WIPP brine B)⁵, a simulated air-free granitic ground water¹¹ prepared by dissolving the components in boiled-distilled water and then bubbling CO₂ into the solution until the precipitate dissolved (the solution was kept under argon but even so the Fe⁺⁺ slowly oxidized and precipitated as hydrated Fe₂O₃), and boiled-distilled water equilibrated with Snake River Plain basalt and in contact with excess solid basalt. The compositions of the leachants are given in Table II; the WIPP brine B and the carbonate water compositions are calculated from their ingredients, while the basalt equilibrated water composition was determined by inductively coupled plasma emission (ICP) analysis. The leach tests with the basalt equilibrated water were always made in the presence of coarse ground basalt with an area of ~50 cm² for tests below 100°C and ~20cm² for tests above 100°C.

The leach tests in the gamma field, ~10⁴ Gy/h (10⁶ Rad/h), were made in radiation resistant containers, stainless steel for the distilled water and Pyrex glass for the other leachants.⁶ The gamma facility consisted of a dry aluminum tube placed in the Advanced Test Reactor (ATR) canal and surrounded by an array of spent ATR fuel elements. The tests were made in a sealed thin-walled stainless-steel can which was purged with argon to exclude air. Gamma heating kept

the leachant temperature between 30°C (minimum field) and 50°C (maximum field). The gamma field was measured with an ionization chamber every time the fuel elements were changed. The total dose was estimated by multiplying the log mean of the initial and final gamma fields by the exposure time.⁶ Because the gamma fields varied with time and position, the total doses are only known to ± 20%.

For distilled water, the tests in the absence of the gamma field were run in MCC-1 specified Teflon jars,²⁰ with Teflon baskets to hold the specimens, and for the other leachants in the Pyrex test tubes. The comparison samples were kept in a laboratory oven maintained at the same temperature, ±2°C, as the samples in the gamma facility. The hydrothermal leach tests were run in 23mL Teflon lined Parr acid digestion bombs^a at 170°C and 250°C. The samples were placed on a Teflon screen just above the bottom of the liner.

For all the tests except the hydrothermal, a volume of leachant in cm³ equal to ten times the sample surface area in cm² was used; for the hydrothermal tests the volume to area ratio was a little lower, as low as seven cm, because of the limited volume of leachant that could be used in the bomb. The Soxhlet tests were made in Pyrex extractors operating at 95°C (normal boiling point at INEL). The tests in 1M CH₃COOH-0.1M CH₃COONa buffer were run in Teflon jars.

For those tests patterned after MCC-1,²⁰ at the conclusion of the leach period the tubes were weighed to check for leachant evaporation, then opened and the samples removed, rinsed, dried and weighed to determine weight loss. The pH of the leachate was determined, then the leachate plus sample rinses were made ~2% in HNO₃ (distilled water) or HCl (other leachates) and returned to the leach container and digested overnight at 90°C. After digestion, the leachate was transferred to a polystyrene counting bottle and the volume made up to 50mL with rinses of the leach container. The 50mL of solution was then counted on the 1-cm shelf of the standardized Ge(Li) gamma spectrometer.

For those tests patterned after the IAEA test,²¹ the sample was removed, rinsed into the old leachate, then, without drying, inserted into fresh leachant and the test continued. The old leachate was then added to the counting bottle, diluted to 50 mL, and counted. Only after the final leach period was the specimen dried and weighed to determine weight loss.

The relative counting efficiencies of the nuclides in the leach specimens and in solution were determined by counting the same amount of tracers on a thin glass sheet at 9cm and in 50mL of solution at 1cm.

For the Soxhlet tests 150mL of distilled water was used. After each period, the flask was removed and a new flask substituted and the test continued. The leachate was then made ~2% in HNO₃, digested, and then a known fraction taken, made up to 50mL, and counted. Only after the final period was the sample weighed to determine weight loss.

For the tests in basalt equilibrated water where solid basalt was present, the basalt was rinsed three times with about 5mL distilled water, then dried, mounted, and counted on the 1cm shelf of the Ge(Li) spectrometer to determine adsorbed activity. The rinses were added to the leachate before counting.

a. #4749 General Purpose Digestion Bomb from Parr Instrument Co., 211 53rd St. Moline, IL 61265

A few distilled water leachates, after acidification and counting, were analyzed for Al, Ca, Na, Si, Li, B, Mg, and Fe by ICP or atomic absorption (AA). Because of iron from stainless steel corrosion, no iron analyses were made on gamma irradiated leachates.

LEACH RATES

Weight loss leach rates were determined by dividing the weight loss by the measured sample area and the leach time. The standard deviation of the leach rates can be estimated from a ± 10 μg uncertainty in the weight loss and a $\pm 10\%$ uncertainty in the area. The elemental leach rates of sodium, cobalt, zirconium, niobium, barium, cesium, cerium, and americium were determined from the Ge(Li) gamma peak counting rates. The fraction leached was calculated by dividing the gamma photopeak counting rate (corrected for background and decay) from the 50mL of solution counted on the 1-cm shelf by the relative counting efficiency and the gamma photopeak count rate of the leach specimen at 9 cm (corrected for background, decay, and gamma self absorption). The leach rate was then determined by multiplying the fraction leached by the specimen weight and dividing by the area and the time. The standard deviation of the leach rate can be estimated from a $\pm 10\%$ uncertainty in the sample area and efficiency ratio, and the counting statistics. The activities were assumed to be uniformly distributed in the acidified leachate solutions. The leach rates from the ICP-AA analyses were also calculated from the fraction leached (total weight in leachate divided by total weight in specimen as calculated from the composition). The leach results assume a uniform melt and no loss of element or gain of aluminum during melting.

The leach rates in distilled water are given in Table III, in salt brine in Table IV, in reducing-carbonate water in Table V, in basalt equilibrated water in Table VI, and for Soxhlet and in the acetate buffer in Table VII. The detection limits (2σ) for a 30-d leach period are about 0.02 $\mu\text{g}/\text{cm}^2\cdot\text{d}$ for Co, Cs, and Am; 0.04 $\mu\text{g}/\text{cm}^2\cdot\text{d}$ for Na, Ba, and Ce; 0.1 $\mu\text{g}/\text{cm}^2\cdot\text{d}$ for Nb and weight loss, and 0.3 $\mu\text{g}/\text{cm}^2\cdot\text{d}$ for Zr. The detection limits are lower for the long-lived spikes for the longer leach periods, but as high or higher for Nb and Zr due to decay. Niobium activity in the leachates can result from Zr decay, so for those cases where the Nb leach rate was not much greater or less than the Zr leach rate, the Nb values are less than the values calculated. Most leach tests showed no detectable Zr ($<2\sigma$), but leach tests in a gamma field often showed Nb.

DISCUSSION OF RESULTS

Effect of Gamma Radiation on Leaching

The leach rates in air-free distilled water increased much less in the gamma field than the rates did in aerated water.⁶ The pH of the air-free water was unchanged by the gamma field as was expected since there was no nitrogen or free oxygen to form nitric acid. The gamma irradiation of the air-free water did result in a small but measurable increase in leach rates, especially for Nb, Ce, Am, Al, Ca, Mg, and Si. In the absence of a gamma field, air-free and aerated water were equivalent leachants (see Fig. 1), the leach rates in 40°C air-free water were about twice those in 30°C aerated water⁶ as would be expected from the 10°C difference in temperature. The leach rates tended to decrease with increasing leach time. The increase in leaching was also about the same in salt brine,⁶ reducing carbonate water and basalt equilibrated water. The pH of the reducing carbonate water and the basalt equilibrated water was not changed by the

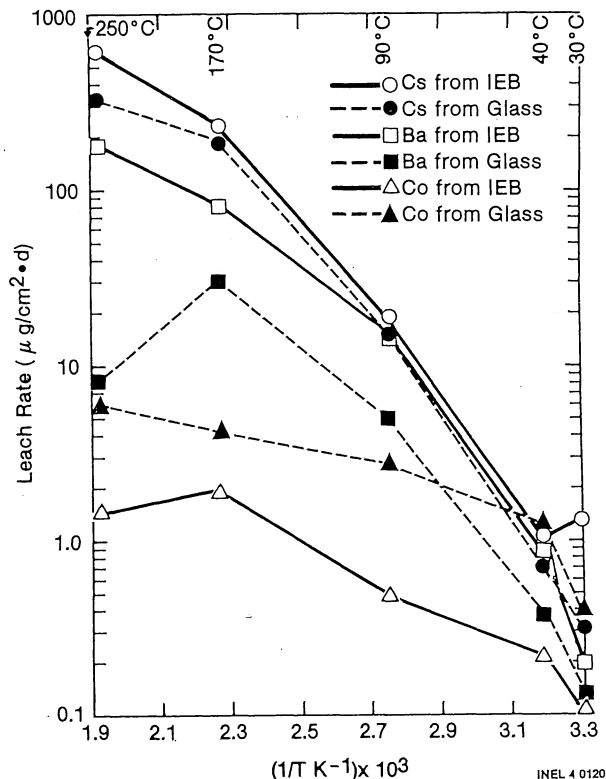


Fig. 1. Variation of leach rates in distilled water versus reciprocal of temperature.

gamma irradiation. If radiolysis of the carbonate water produced organic acids,^{12,13} the acids were neutralized by leached alkali. The leach rates in the reducing carbonate water were about the same as those in air-free water and again tended to decrease with time. The lowest leach rates were observed in air-free distilled water equilibrated with basalt and in contact with basalt. Much of the leached activity was adsorbed on the basalt. Some earlier leach experiments in granite equilibrated water containing solid granite also showed a very low rate for Cs leaching into the solution.⁴ Except for cobalt, both waste forms were about equally durable both in and out of the gamma field; cobalt was always much less leachable from IEB.

Effect of Temperature on Leaching

For most elements, an increase in temperature caused a marked increase in leaching; however, for Ba leaching from glass into distilled water, the 250°C leach rate was less than the 170°C leach rate, see Fig. 1. Earlier leach tests had also shown a decrease in leaching of certain elements with increasing temperature.^{3,4} The increase with temperature of Na, Cs, and Ba leach rates was usually somewhat greater for IEB than glass; however, cobalt remained much less leachable from IEB, see Fig. 2. Leach rates at 170°C and 250°C were the lowest (except for Ba in hydrothermal water) in basalt equilibrated water containing basalt. In hydrothermal salt brine, Na, Cs, and Ba all had nearly the same leach rates, see Fig. 2. The high hydrothermal leach rates of Na and Cs from IEB into reducing carbonate water may have been due to carbonate complexing or perhaps to precipitated hydrated Fe_2O_3 .²² The hydrothermal leach rates of Zr, Nb, Ce, and Am were almost always less than their detection limits of 2-10 $\mu\text{g}/\text{cm}^2\cdot\text{d}$.

TABLE III

Leach Rates in Air-Free Distilled-Deionized Water, $\mu\text{g}/\text{cm}^2 \text{ d}$

Temp. °C	40	40	42	42	40	40	90	90	90	90	90	170	250
Time-Days	29	29	67	67	133	133	28	35 ^a	105 ^a	139 ^a	175 ^a	6.92	7.0
γ -Dose, Gy	9.5E6	0	2.45E7	0	4.3E7	0	0	0	0	0	0	0	0

Iron-Enriched Basalt

Na	3.3	1.02	3.0	1.63	1.20	0.84	16.2	13.0	6.4	5.3	4.2	240	780
Co	0.216	0.212	0.21	0.156	0.082	0.053	0.39	0.16	0.055	0.10	0.048	1.96	1.4
Zr	b	b	b	b	b	b	b	b	b	b	b	b	b
Nb	b	b	0.20	b	b	b	b	b	b	b	b	b	b
Cs	1.10	1.02	3.4	1.70	1.11	0.93	19	14.4	7.4	6.0	4.8	243	640
Ba	2.6	0.83	3.8	1.56	0.92	0.76	15.7	14.4	6.4	5.1	3.6	85	190
Ce	0.19	b	0.26	0.15	0.12	0.08	b	b	b	b	b	b	b
Am	0.26	b	0.48	0.10	0.13	0.036	b	b	b	b	b	b	b
Al	2.9	1.46	3.5	2.0	1.18	0.86	-	-	-	-	-	-	-
Ca	3.6	1.59	1.39	2.1	0.45	0.40	-	-	-	-	-	-	-
Mg	0.84	0.80	0.67	1.29	0.15	0.18	-	-	-	-	-	-	-
Si	2.45	1.20	1.49	1.66	0.80	0.66	-	-	-	-	-	-	-
Fe	-	0.11	-	0.18	-	0.19	-	-	-	-	-	-	-

Weight-Loss	1.6	0.75	1.8	1.04	0.55	0.46	-	-	-	-	3.04 ^c	118	269
Final pH	7.1	7.3	7.1	7.4	7.4	7.6	8.5	7.9	7.6	7.3	7.6	7.1	8.9

Glass

Na	6.1	1.15	3.8	3.1	1.88	1.32	15.9	14.8	5.9	4.3	3.5	205	520
Co	1.28	1.40	1.43	0.63	0.67	0.81	2.74	0.32	0.40	0.37	0.40	4.2	6.1
Zr	b	b	b	b	b	b	b	b	0.63	b	b	b	b
Nb	1.1	b	0.30	b	0.24	b	b	b	1.0	b	b	b	b
Cs	6.2	0.69	4.5	3.3	2.25	1.32	15.7	15.1	6.0	4.5	3.6	196	328
Ba	3.8	0.38	2.8	1.32	1.41	0.39	5.0	5.4	1.44	1.04	0.82	30	8
Ce	b	0.14	0.13	b	0.10	b	b	b	0.48	b	0.15	b	b
Am	1.5	0.14	1.3	0.04	0.62	b	b	b	0.31	b	0.11	b	b
Al	-	-	-	-	4.90	3.05	-	-	-	-	-	-	-
Ca	-	-	-	-	2.20	0.90	-	-	-	-	-	-	-
Mg	-	-	-	-	2.82	1.72	-	-	-	-	-	-	-
Si	-	-	-	-	1.45	1.14	-	-	-	-	-	-	-
B	-	-	-	-	2.36	1.61	-	-	-	-	-	-	-

Weight-Loss	6.2	0.74	4.1	3.9	1.85	1.13	-	-	-	-	4.98 ^c	142	240
Final pH	7.4	6.8	6.5	7.2	7.7	7.8	9.3	8.5	8.6	8.4	8.3	7.5	8.3

a. Continued leach on same sample.

b. Leach rate less than detection limit.

c. Leach rate for 482d.

TABLE IV
Leach Rates in Salt Brine $\mu\text{g}/\text{cm}^2\cdot\text{day}$

Time-Days	28	28	63	63	126	126	28	35 ^a	105 ^a	139 ^a	175 ^a	7	7
Temp. °C	30	30	30	30	30	30	90	90	90	90	90	170	250
Y-Dose, Gy	5.2E6	0	1.6E7	0	3.1E7	0	0	0	0	0	0	0	0
Iron Enriched Basalt													
Na	1.85	1.91	1.82	1.83	0.90	1.22	25	7.1	3.1	2.06	1.65	310	810
Co	0.054	0.083	0.064	0.032	0.043	0.013	0.28	0.20	0.026	0.011	0.013	6.6	7.5
Zr	b	b	b	b	b	b	b	b	b	b	b	b	b
Nb	0.07	0.15	b	b	0.05	b	b	b	b	b	b	b	b
Cs	0.21	0.27	0.41	0.15	0.14	0.03	4.8	4.9	1.95	2.02	1.73	165	690
Ba	0.20	0.16	0.17	0.08	0.113	0.038	5.2	5.0	2.0	2.1	1.65	175	660
Ce	b	b	b	b	0.044	b	b	b	b	b	b	26	b
Am	1.9	0.33	0.73	b	0.22	b	b	b	b	b	b	12	b
Weight-Loss	0.30	gain	0.06	gain	0.11	gain	-	-	-	-	0.32 ^c	54	179
pH	-	5.9	4.4	6.8	4.0	6.6	5.7	7.0	7.6	6.6	6.5	5.3	6.4
Glass													
Na	1.02	0.82	0.18	0.085	0.44	0.33	3.3	2.4	1.17	0.87	0.57	119	500
Co	0.88	0.59	0.34	0.08	0.28	0.21	2.51	0.21	0.076	0.063	0.10	74	138
Zr	b	b	b	b	b	b	b	b	b	b	b	b	b
Nb	0.08	0.09	b	b	b	b	b	b	b	b	b	b	b
Cs	0.76	0.56	0.091	b	0.28	0.22	2.7	2.4	1.14	0.92	0.63	100	455
Ba	0.97	0.61	0.10	0.078	0.40	0.24	3.4	3.0	1.25	0.99	0.61	103	420
Ce	b	b	b	b	b	b	b	b	b	b	0.055	b	b
Am	0.56	b	0.23	b	0.07	b	b	b	b	b	0.06	1.1	b
Weight-Loss	0.40	0.62	0.62	0.30	0.12	0.10	-	-	-	-	0.50 ^c	62	233
pH	-	-	5.0	6.3	6.7	6.5	5.9	6.7	7.7	6.9	6.7	5.3	6.3

- a. Continued leach on same sample.
b. Leach rate less than detection limit.
c. Leach rate for 482d.

TABLE V

Leach Rates in Reducing Carbonate Water $\mu\text{g}/\text{cm}^2\text{-day}$

Time-Days	29	29	67	67	133	133	31	7	7
Temp. °C	40	40	42	42	40	40	90	170	250
γ -Dose Gy	9.5E6	0	2.45E7	0	4.3E7	0	0	0	0
Iron-Enriched Basalt									
Na	5.6	2.54	3.5	1.0	1.75	2.20	33.4	340	1780
Co	0.17	0.098	0.12	0.113	0.107	0.027	0.38	0.98	1.4
Zr	a	a	a	a	a	a	a	a	a
Nb	0.74	a	a	a	0.28	a	a	a	a
Cs	2.8	0.79	1.93	0.82	0.85	0.62	33.3	306	1660
Ba	2.12	0.54	1.82	0.64	0.72	0.33	31	48	270
Ce	a	a	a	0.09	0.10	a	a	a	a
Am	0.30	a	0.14	0.08	0.17	a	a	a	a
Weight-Loss	0.84	0.16	0.85	0.42	0.28	0.26	13.2	132	678
pH	6.9	6.8	6.7	7.0	7.5	7.7	6.8	6.9	6.9
Glass									
Na	2.3	1.15	3.04	0.95	1.19	0.26	27.8	111	640
Co	2.1	1.28	2.25	0.80	0.88	0.36	10.0	3.38	65
Zr	a	a	a	a	a	a	a	a	a
Nb	0.83	a	2.5	0.69	0.64	a	a	a	a
Cs	2.0	0.65	2.8	0.77	0.98	0.16	28.9	107	530
Ba	1.77	0.68	2.33	0.69	0.68	0.18	13.6	44	83
Ce	a	a	1.6	0.49	a	0.059	a	a	a
Am	0.86	0.04	1.5	0.38	0.30	0.04	a	a	a
Weight-Loss	2.0	0.68	2.4	0.63	0.69	0.13	20.8	51	350
pH	6.7	7.4	7.3	7.5	8.0	8.0	7.7	8.1	7.2

a. Leach rate less than detection limits.

TABLE VI

Leach Rates in Basalt Equilibrated Water Leading to Activity in Solution and on Basalt, $\mu\text{g}/\text{cm}^2\text{-day}$

Temp. °C	35 (9×10^6 Gy)		35		90		170		250	
	In Sol.	Basalt	In. Sol.	Basalt	In Sol.	Basalt	In Sol.	Basalt	In Sol.	Basalt
Time-Days	31	31	31	31	31	31	7	7	7	7
Iron-Enriched Basalt										
Na	0.50	0.15	0.13	0.043	1.45	2.53	22.8	74	130	380
Co	0.064	0.113	0.025	0.015	0.054	0.051	0.94	2.55	0.85	0.24
Zr	a	a	a	a	a	a	a	a	a	a
Nb	a	a	a	a	a	a	a	a	a	a
Cs	0.079	0.21	0.026	0.038	0.094	0.43	26	15.7	167	121
Ba	0.13	0.23	a	0.027	0.11	0.84	9.9	62	34	103
Ce	a	0.31	a	a	a	a	a	a	a	a
Am	0.16	0.34	a	a	0.029	0.022	a	a	a	a
Weight-Loss	0.28	-	gain	-	0.09	-	17.9	-	54	-
pH	7.0	-	6.6	-	7.0	-	6.3	-	7.0	-
Glass										
Na	0.65	0.25	0.24	0.11	0.41	1.01	10.4	33	73	186
Co	0.13	1.35	0.14	0.34	0.21	1.21	2.34	9.0	2.11	1.58
Zr	a	a	a	a	a	a	a	a	a	a
Nb	a	a	a	a	a	a	a	a	a	5.1
Cs	0.089	0.41	a	0.094	0.11	0.57	14.2	9.1	17.2	23.4
Ba	0.18	0.64	0.063	0.1	0.11	0.75	3.0	19	1.8	30
Ce	a	0.31	a	a	a	a	a	a	a	a
Am	0.083	0.21	a	a	a	0.017	a	a	a	a
Weight-Loss	0.28	-	a	-	0.13	-	8.5	-	a	-
pH	7.4	-	6.8	-	7.3	-	7.4	-	8.0	-

a. Leach rate less than detection limit.

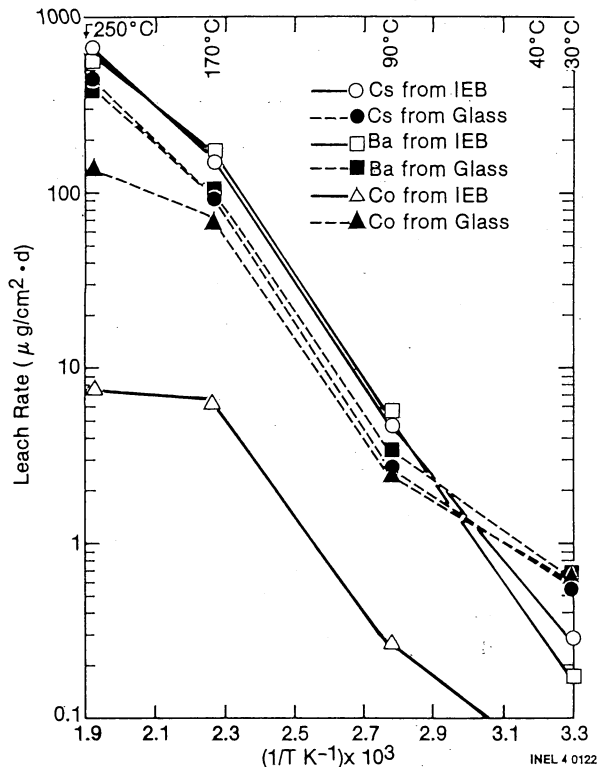


Fig. 2. Variation of leach rate in salt brine versus reciprocal of temperature

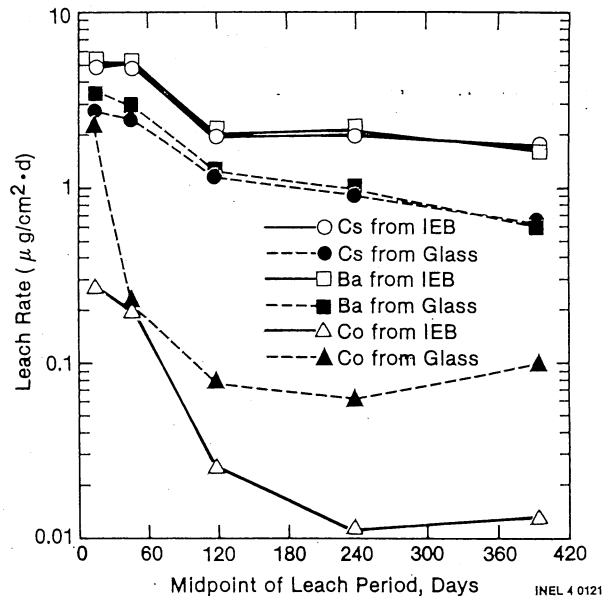


Fig. 3. Variation of leach rate in salt brine versus time. IAEA test 90°C.

gamma radiation field produced by the waste should cause only a small (about twofold) increase in leach rates. The use of radioactive tracers greatly simplifies the determination of leach rates in the simulated repository leachants.

Miscellaneous

Leach rates were measured on glass and IEB in 90°C distilled water and salt brine following the IAEA leach test, see Fig. 3. The leachant was changed after 28d, then 35d, 105d, 139d, and finally 175d. The leach rates decreased with time. The total amount leached during the 105d 3rd period, 139d 4th period, and 175d 5th period were almost the same indicating saturation, while for the initial 28d and 35d periods the total amounts leached were usually a little less. Long-term MCC-1 leach tests have also shown this saturation effect.²³ The sodium leached from IEB into brine during the first period was quite high, indicating a high surface concentration of sodium in the solid or rapid exchange between the solid and the brine. Continued Soxhlet leaches and leaches in 1.0M CH₃COOH - 0.1M CH₃COONa buffer also showed a decrease of leach rate with time, although the total amount leached was greater for the later long leach periods. Glass was much more leachable in the CH₃COOH - CH₃COONa buffer than IEB, while both waste forms were roughly equally leachable (except for Co) in the Soxhlet tests. Both glass and IEB are more leachable in the pH 3.8 CH₃COOH - CH₃COONa buffer than in irradiated aerated water where the pH was usually lower, indicating the acetate increased leaching as well as the acidity. The acetate buffer leached most of the elements almost equally, indicating congruent dissolution.

CONCLUSIONS

The tests showed that leaching in simulated leachants is little different for the INEL waste forms than leaching in the distilled water recommended for the MCC-1 tests. The effect of gamma radiation on leaching is also about the same for all the leachants used except aerated water where radiolytic nitric acid increased the leaching considerably. Since most ground waters in crystalline rock repositories are expected to be air-free (after the repository is closed), the

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TABLE VII

Leach Rates in Acetate Buffer and Soxhlet Leach Rates $\mu\text{g}/\text{cm}^2 \cdot \text{day}$

Leachant Temp. °C Time-Days	1M CH ₃ COOH, 0.1M CH ₃ COONa						Soxhlet-Distilled Water		
	40 3	40 25 ^a	40 72 ^a	90 3	90 25 ^a	90 72 ^a	95 3	95 11 ^a	95 49 ^a
Iron-Enriched Basalt									
Na	46	23	13.8	260	80	42	184	108	73
Co	10	4.5	3.49	58	15.0	8.1	12.4	3.7	2.4
Zr	b	b	12	40	19	22	b	b	b
Nb	b	b	(5.2) ^d	(26) ^d	(17) ^d	(24) ^d	b	b	b
Cs	45	24	15.0	280	89	48	198	120	72
Ba	48	26	15.2	270	85	45	179	100	76
Ce	50	26	14.7	290	90	47	6.6	b	b
Am	57	28	16.4	340	100	52	b	b	b
Weight Loss	-	-	13.0 ^c	-	-	49.3 ^c	-	-	50 ^c
Glass									
Na	690	109	43	390	170	82	147	104	83
Co	650	93	37	390	174	82	228	104	101
Zr	270	65	30	210	160	88	b	b	b
Nb	(220) ^d	(27) ^d	(28) ^d	(210) ^d	(150) ^d	(60) ^d	b	b	5.6
Cs	670	109	42	400	180	87	108	86	64
Ba	690	101	39	400	180	83	141	95	81
Ce	700	106	42	400	180	86	b	b	4.6
Am	660	93	46	450	240	85	b	b	4.0
Weight Loss	-	-	68.4 ^c	-	-	106 ^c	-	-	87 ^c

a. Continued leach on same sample.
c. Leach rate for total leach time.

b. Leach rate less than detection limit.
d. Nb leach rates \leq above values because of Nb from Zr decay.