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ABSTRACT

SRP glass containing actual radioactive waste was leached in static tests at 90°C in a tuffaceous groundwater (J-13 water at pH ~7.4) at a SA/V ratio of $100m^{-1}$ in 316 stainless steel vessels. Tests were performed for time periods up to 134 days. Normalized mass losses were calculated for Cs-137, Sr-90, and Pu-238. The Cs-137 in the leachate appeared to reach a steady value of ~3 g/m^2, corresponding to a steady-state concentration of only 1.0 ppb for total cesium. The mass losses based on Sr-90 and Pu-238 appearing in solution were low (<0.3 and <0.01, respectively) because of their low solubilities. However, significant amounts of these radionuclides had deposited on the steel vessel while the amount of deposited Cs-137 was negligible. During the leach tests, the pH changed <0.4 units and the only significant effect of radiolysis was reduction of NO_3^- ions in solution to NO_2^-. When compared to earlier tests, the results confirm that leach rates in the earlier tests with radioactive glass in Teflon® (product of Du Pont) vessels were high due to radiolysis of the Teflon®. The results also indicate that radioactive and nonradioactive glasses of comparable composition and surface finish leach essentially identically.

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INTRODUCTION

Savannah River Laboratory (SRL) is evaluating the performance of Savannah River Plant (SRP) high-level nuclear waste borosilicate glass in a tuff repository environment. The volcanic tuff beds of Yucca Mountain, Nevada are being investigated as a repository for the permanent storage of nuclear waste. As part of the evaluation by SRL, borosilicate glass containing actual SRP radioactive waste, and glass containing nonradioactive simulated waste were leached in a water-saturated tuff environment.[1,2] Water saturation represents a worst possible case since the repository horizon will be in the unsaturated zone and the amount of water will be limited.[3] In the saturated tests,[1,2] results were obtained in actual tuff groundwater (J-13 water) in Teflon® leach vessels in the presence and absence of tuff rock. Conclusions were that tuff rock lowers the concentrations of radionuclides (Cs-137, Sr-90, and Pu-238) leached from radioactive glass and that radioactive and nonradioactive glass leach similarly.

In the long-term tests with radioactive glass in the absence of rock, it appeared that radiolysis of the Teflon® vessel was increasing the dissolution of the glass.[2] High concentrations of Li and B ions from the glass appeared in these leachates along with F^- ions from the vessel. Even though it had been shown that radiolysis of the Teflon® could enhance leaching,[4] it was not expected to be a factor in that study since most of the radiation from the glass (beta radiation from Sr-90 and Y-90) was absorbed by the J-13 water and not by the Teflon® vessel.

To obtain a true measure of the leaching of radioactive glass in small volumes of tuff groundwater, the above tests in the absence of tuff rock were repeated using stainless steel (SS) leach vessels. Stainless steel vessels have been used previously in leach tests where the effect of gamma radiation on leaching in J-13 water was investigated.[5,6] In those tests, the steel vessel was not a significant factor affecting the leaching of the glass. The

results summarized here are for leach tests in J-13 water at SA/V = $100m^{-1}$ at 90°C for up to 134 days. The results are compared to the earlier results obtained in Teflon® vessels with radioactive glass and with nonradioactive glass. Detailed procedures, results, and solution concentrations are presented elsewhere.*

EXPERIMENTAL PROCEDURES

Radioactive Glass Preparation and Composition

The glass was the same as that used in earlier tests with J-13 water and Teflon® vessels.[1,2] It was prepared in a slurry-fed, joule-heated melter that was operated remotely in the Shielded Cells Facility (SCF) at SRL. Nominal composition of the glass was 28 wt % radioactive waste from SRP waste tank 42 and 72 wt % frit 165. The waste-frit mixture was melted at 1150°C and poured into thin-wall 304L stainless steel steel cylinders 1.8 cm O.D. These were then sliced to produce 2-mm-thick disks for leaching. SEM microscopy indicated that the glass contained less than 1 vol % crystals which were identified as ferrite spinels.

For this study, the composition of the glass was redetermined using HF/HCl dissolution procedures developed for application in the SCF. The measured composition based on three different samples (Table 1) agreed within 10% of that determined in an earlier study[1,2] except that the wt % Li_2O was 25% lower in the redetermination. This lower result for Li_2O is more in line with that expected from the known composition of the melter feed. Based on the lower result for Li_2O, the normalized mass losses for lithium presented in References 1 and 2 should be increased by a factor of 1.3. All the other results in those References are unchanged.

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* N. E. Bibler, "Leaching Radioactive SRP Nuclear Waste Glass in Tuff Groundwater in Stainless Steel Vessels," USDOE Report, to be published.

The measured dose rate from the surface of glass was 1300 rad/hr. This was accurately determined using calibrated thin film radiochromic dosimeters[7] that were placed directly on the glass. The dose rate from the glass is due primarily to the beta particles from Sr-90 and its daughter Y-90.

Leaching Procedures

A 304L SS basket was used to suspend the glass disks in the 316 SS Parr reaction vessels (capacity = 22 mL). The vessels were sealed with a compression fitting and a Teflon® gasket that provided a leak-free system. The vessels and baskets were cleaned with ethanol and 1M nitric acid. Blank leach tests at 90°C indicated that leaching from the vessels and baskets was negligible compared to that from the glass.

The glass disks (banded with 304L SS) were polished remotely to 600 grit surfaces. Examination of the surfaces by a magnifying periscope in the SCF indicated that, because the operations were performed remotely, the surfaces were not completely level; thus, the entire surface was not 600 grit. This nonuniformity of the surface finishes probably caused much of the scatter in the data observed in the earlier tests[1,2] and in the tests reported here. After the glass disks were polished, they were cleaned according to MCC-1 procedures. Two disks separated by spacers of 304L SS were used for each test. The total surface area of glass was 9.4 cm^2; thus, to obtain a SA/V ratio of $100m^{-1}$, 9.4 mL of J-13 water were used. After the vessels were filled and sealed, they were put into an oven at 90° $\pm$ 0.5°C in the SCF.

J-13 water is a tuffaceous groundwater that contains 0.04, 0.14, 27, and 42 ppm of Li, B, Si, and Na. Principal anions are HCO_3^- and $SO_4^=$.

After each test, the reaction vessel was removed from the oven and allowed to cool to ambient temperature. It was then opened, and the basket and glass were removed. The vessel was immediately resealed. The glass was dumped from the basket and the basket placed in a noncontaminated plastic vial. The vial and reaction

vessel were removed from the SCF to a radioactive hood where the remaining procedures could be performed by hand rather than remotely. The vessels were opened and the solution removed and weighed so its volume could be accurately determined. Aliquots were then removed from the solution for pH determination and other analyses.

Nonradioactive cations were determined by inductively coupled, plasma induced spectroscopy of acidified aliquots, anions by ion chromatography, and radionuclides by calibrated counting techniques. Radionuclides that had sorbed on the basket and the Parr reaction vessel were determined by leaching the containers several times for 16 hours with 1M nitric acid at 90°C or until no further radioactivity was detected in the leachates.

RESULTS AND DISCUSSION

All tests were done in duplicate except that for 91 days. Results for leaching Cs-137, Sr-90, and Pu-238 from the glass for all the tests are presented. Results are also presented here for pH changes and anion concentration changes in the tests.

Leach results are presented in terms of normalized mass loss given by $NL_i = N_i/(SA \times X_i)$, where NL_i is the mass of glass dissolved per unit area based on species i. N_i is the amount of species i measured, SA is the surface area of the glass, and X_i is the mass fraction of i in the glass. Two types of NL_i values are given. One, $NL_{i,soln}$, is based on the amount of i detected in the leachate itself as either being soluble or as part of suspended particulates that were sampled with the solution. The other, $NL_{i,total}$, is based on the total amount of i leached from the glass. This includes the amount of i that was sorbed or deposited on the steel basket or vessel.

Leach Results for Cs-137

Values for both $NL_{i,soln}$ and $NL_{i,total}$ based on Cs-137 are shown in Figure 1. Average results for leaching Cs-137 with

Teflon® vessels[1,2] are included in Figure 1 for comparison. Even though the Cs-137 results are scattered, they are in general agreement with the results determined earlier in Teflon® leach vessels. It appears that, based on the results in Teflon®, a long-term steady-state concentration of cesium is being approached. The average value for $NL_{Cs-137,soln}$ for all the results in Figure 1 for tests longer than 14 days, including those for Teflon® vessels, is 2.7 ± 0.5 g/m^2. Other workers have found that cesium approaches a constant concentration when leaching SRP glass in deionized water[8,9] or in a synthetic silicate groundwater.[9]

For the average normalized mass loss of 2.7 g/m^2, a steady-state concentration of Cs-137 is calculated to be 0.4 ppb from the specific activity of Cs-137 and the Cs-137 content of the glass. The ratio of Cs-137 to total cesium in the glass is approximately three thus, the total concentration of cesium in the J-13 water is 1.0 ppb. This is a low concentration for Cs when compared to the solubility of typical Cs compounds. The concentration in solution appears to be controlled by a sorption or precipitation process occurring in the altered layer of the glass. More evidence for this will be presented later.

Leach Results for Sr-90 and Pu-238

Results for Sr-90 and Pu-238 (Table 2) indicate large differences between NL_{soln} and NL_{total} suggesting that the concentration of these radionuclides in the leachate is limited by their solubility. The large scatter in the results for NL_{soln} for both radionuclides can be partially attributed to the presence of insoluble particulates in the nonacidified leachates leading to nonrepresentative sampling.

The low values for NL_{soln} for Sr-90 in these tests (0.1 g/m^2) is consistent with the values determined by Bates[6,8] and Strachan.[9] In those studies, the Sr concentration decreased as the leach time increased, presumably due to the pH increase caused by the leaching process. A consistent decrease was not evident in this study,

probably because the pH did not increase significantly with leach time.

For Pu-238, nearly all the Pu-238 that was detected was on the steel and not in the solution. This behavior is typical for plutonium. For example, Bates found three times more plutonium had sorbed on the steel vessel than appeared in solution.[6] The value for NL_{total} for Pu-238 in Table 2 is essentially constant at 0.3 g/m^2 and is consistent with the range of 0.5-0.8 determined by Bates[6] at a lower SA/V ratio of 10 m^{-1}.

pH Changes and Anion Concentrations

The pH values and anion concentrations in the J-13 water before and after the leach tests are shown in Table 3. The dose rate to the solution during leaching was probably in excess of 2000 rad/hr since four surfaces of glass were exposed. The total dose to the solution in the longest test was ~10^7 rads.

The pH changes were slight even though both leaching and radiolysis were occurring. Leaching causes the pH to increase and radiolysis could cause it to decrease. When nonradioactive glass was leached in J-13 water, the pH increased to 9.0 in leach tests longer than 28 days due to alkali ions being released from the glass.[1,2] Radiolysis would cause the pH to decrease due to nitric acid formation if moist air in the vessel is irradiated.[10] In leach tests in a gamma radiolysis facility where the air was definitely irradiated[6], the pH decreased to 6.4 during leaching. In the tests discussed here with radioactive glass, most of the beta radiation is being sorbed by the water and the dose to the air is not significant.

It is definite that a small amount of F^- was produced during the tests from the Teflon® gasket. Nitrite was definitely produced during the tests while the nitrate was reduced due to radiolysis of the water.[11] In the three longer tests, a slight amount of oxalate was detected by the IC. This species has been observed in the gamma radiolysis of carbonate groundwaters.[12]

Comparison of Leaching in Stainless Steel and Teflon® Vessels

Leaching results in SS and Teflon® can be compared by the pH and anion changes in the leach tests (Tables 3 and 4) and by the normalized mass losses for Cs-137, Li, and B (Figure 2). Details of the tests in Teflon® are presented elsewhere.[2] In Table 4, the results of leach tests in Teflon® vessels show that large amounts of F^-, Cl^-, NO_2^-, and NO_3^- are produced. Also in these tests, the pH definitely decreases, especially in the longer tests. Fluoride and chloride are produced by radiolysis of the Teflon®. Nitrite and nitrate are produced by radiolysis of the air. Production of these four anions would cause the pH to decrease and leaching to increase.

The data in Figure 2 clearly indicate that in the Teflon® vessels, the glass is dissolving much more rapidly than in SS vessels. Since lithium and boron are soluble in the leachates, they are good measures of the amount of glass that has been dissolved. It is especially significant that, even though the glass is being dissolved much more rapidly in the Teflon® vessels, the normalized mass loss for Cs-137 is still as low as it was in the SS vessels. This is further evidence that the Cs-137 release is being controlled by some reaction in the altered layer of glass. The glass contains aluminum and silicon. Perhaps cesium is reacting with these elements in the altered layer of the glass to produce an alumino-silicate which has a very low solubility.

Comparison of Leaching Radioactive and Nonradioactive Glass

Figure 3 shows the normalized mass losses for lithium and boron for radioactive and nonradioactive glass of similar composition and surface finish. The radioactive results are for the tests in SS and the nonradioactive results for the tests in Teflon®.[1,2] Although the data are scattered, there is general agreement among the results. Exact agreement is not expected because the glasses have slightly different composition and the surface finishes are not exactly equal due to polishing problems with the radioactive glass.

CONCLUSIONS

The data presented in this study support the following conclusions concerning the leaching of radioactive SRP glass in J-13 water.

1. 316 Stainless steel vessels can be used for leaching radioactive glass without introducing effects due to radiolysis of the steel. It should be noted that steel will adsorb significant amounts of Sr-90 and Pu-238.
2. Cs-137 approaches a low steady-state concentration of ~1.0 ppb that may be controlled by formation of alteration products remaining on the surface of the glass.
3. Radiolysis of J-13 water does not significantly affect leaching even in the presence of dissolved air. pH changes are negligible while nitrate in the J-13 water is reduced to nitrite.
4. When the effects due to radiolysis of the leach vessel are nullified and the glasses are of comparable composition and surface finish, radioactive SRP glass and nonradioactive glass with simulated waste leach identically within experimental error.

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TABLE 1

Measured Composition of Radioactive SRP Glass in Three Separate Determinations[a]

Nonradioactive Composition (Weight % Oxide)

Oxide	Wt. %	Oxide	Wt. %
SiO_2	55.4 ± 2.7	Al_2O_3	9.8 ± 0.1
Na_2O	11.0 ± 0.6	Fe_2O_3	6.0 ± 0.3
Li_2O	4.9 ± 0.3	MnO_2	1.9 ± 0.1
B_2O_3[b]	8.4[b]	CaO	0.24
MgO	1.0 ± 0.1	NiO	0.9

Radioactive Composition (mCi per gram glass)

Radionuclide	mCi/g glass	Radionuclide	mCi/g glass
Cs-137	0.111 ± 0.004	Sb-125	0.0099 ± .0005
Sr-90	7.18 ± 0.68	Eu-154	0.045 ± .009
Pu-238	0.042 ± 0.005	Eu-155	0.016 ± 0.001
Zr-95	0.005	Co-60	0.0055 ± 0.0045

[a] Uncertainties are the average deviations. If only one result is presented in the table, only a single analysis was obtained for that element. Dissolution was by conc. HF/HCl, followed by boric acid to complex F^-.

[b] Determined by Na_2O_2 fusion dissolution.

TABLE 2

Normalized Mass Losses (g/m^2) for Sr-90 and Pu-238 Based on Amount in Solution and on Total Amount Leached[a]

Reaction Time, Days	Sr-90				Pu-238			
	1st Test		2nd Test		1st Test		2nd Test	
	Soln.	Total	Soln.	Total	Soln.	Total	Soln.	Total
14	.11	.21	.21	.36	.0047	.39	.012	.34
32	.067	1.1	.10	.82	.0077	.31	.029	.30
56	.087	.57	--	--	.0047	.35	.0049	.31
71	.15	.28	.13	.23	.00034	.25	.0003	.31
91	.57	.86	--	--	.019	.69	--	--
134	.043	.25	.15	.34	.009	.22	--	--

[a] 316 SS Vessels, J-13 Water, T = 90°C, SA/V = $100 m^{-1}$.

TABLE 3

Final pH Values and Anion Concentrations for Radioactive Leach Tests in 316 Stainless Steel Vessels[a]

Leach Time, Days	Final pH	Anion Concentrations, ppm				
		F^-	Cl^-	NO_2^-	NO_3^-	$SO_4^=$
0[b]	7.4	2.0	4.9	0.0	5.6	22.0
14	7.1	5.2	7.4	3.9	2.0	20.0
14	7.1	23.0	6.5	3.4	4.1	24.0
32	7.3	9.8	6.1	4.4	1.7	19.0
32	7.4	3.9	6.0	0.0	0.0	19.0
56	7.2	9.4	2.3	4.9	2.5	28.0
56	7.2	7.1	2.4	1.5	1.8	26.0
71c	7.2	2.5	6.3	3.6	4.0	18.0
71c	7.2	12.0	6.2	4.3	1.0	18.0
91c	7.4	13.0	7.2	7.3	4.7	23.0
134c	7.8	9.4	6.5	6.3	2.0	21.0
134c	7.6	18.0	8.0	0.0	0.0	31.0

[a] $T = 90°C$, $SA/V = 100m^{-1}$, J-13 water; Dose rate to the solution was 1300 rad/hr.

[b] These results agree with measurements at LLNL for J-13 water. Carbonate is also present at ~140 ppm.

[c] $C_2O_4^=$ at ~1 ppm was detected in these leachates.

TABLE 4

Final pH Values and Anion Concentrations for Radioactive Leach Tests in Teflon® Vessels[a]

Leach Time, Days	Final pH	Anion Concentrations, ppm				
		F^-	Cl^-	NO_2^-	NO_3^-	$SO_4^=$
0[b]	7.3	2	6.7	0	6.9	19.1
14	--	19	4.9	10	2.3	9.2
28	7.0	91	17.0	35	3.0	18.2
32	7.0	123	27.0	42	18.0	24.0
56	5.5	186	4.0	37	5.4	20.1
71	6.0	190	--	95	4.8	22.2
91	5.3	196	92.0	116	23.0	16.7
127	6.1	329	c	c	c	25.5

[a] $T = 90°C$, $SA/V = 100m^{-1}$, J-13 water; Dose rate to the solution was 1300 rad/hr.

[b] These results agree with measurements at LLNL for J-13 water. Carbonate is also present at ~140 ppm.

[c] These could not be measured due to the large F^- concentration.

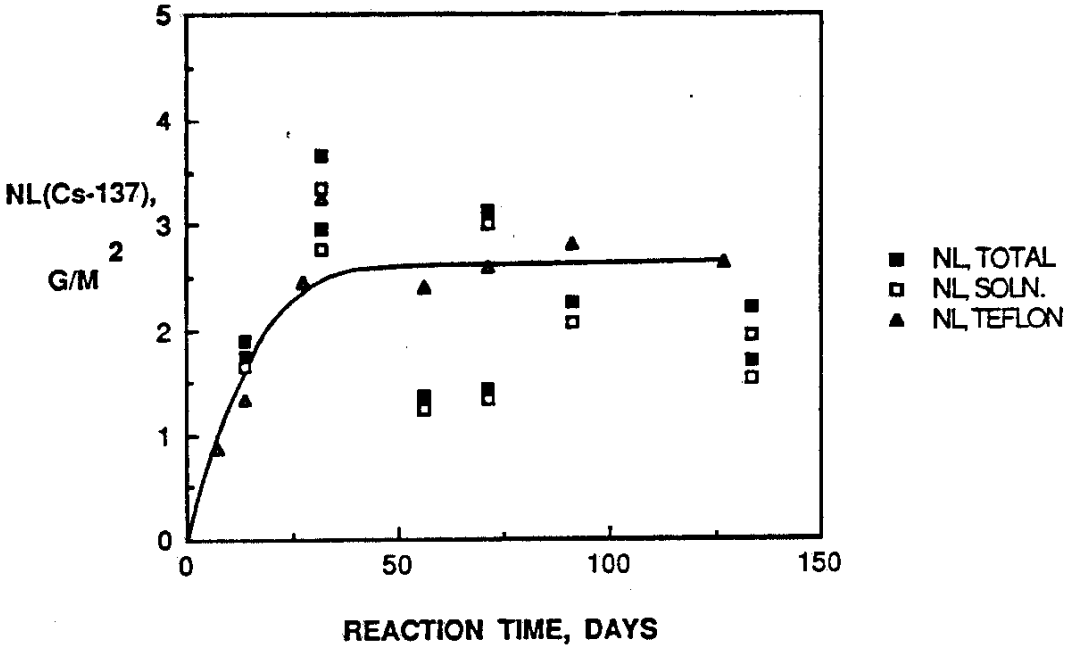

FIGURE 1. Normalized Mass Losses for Cs-137 Based on the Amount Dissolved in the J-13 Water and the Total Leached. Average Results for Cs-137 in Teflon® were used to define the line. T = 90°C, SA/V = 100m^{-1}

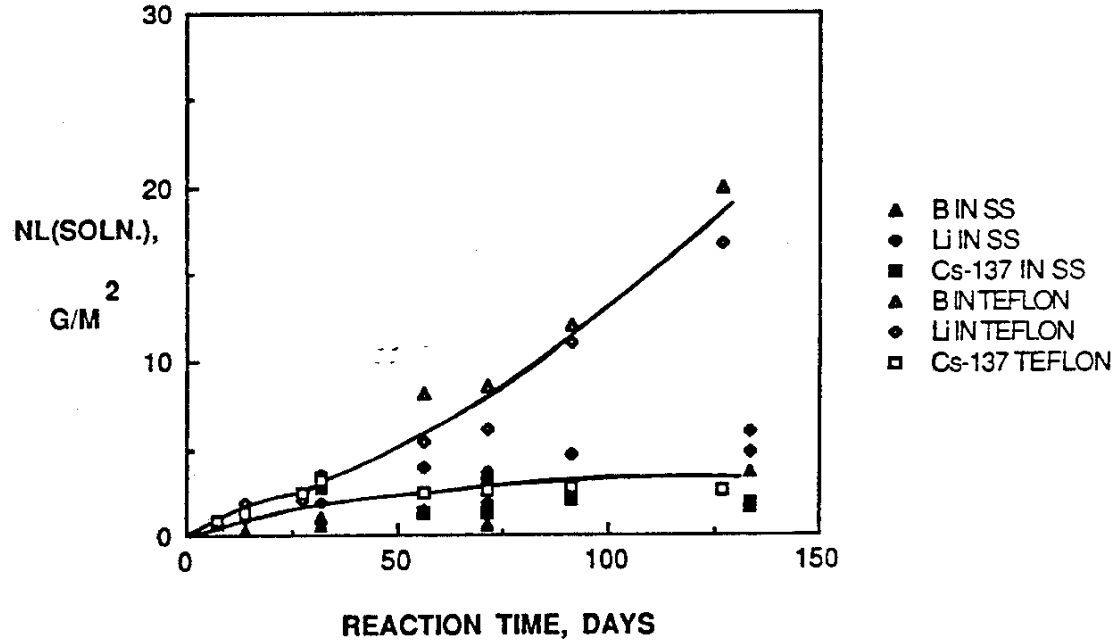

FIGURE 2. Leaching Radioactive Glass in J-13 Water in Stainless Steel and Teflon® Vessels. Lines indicate the Trend of the Data. T = 90°C, SA/V = 100m^{-1}

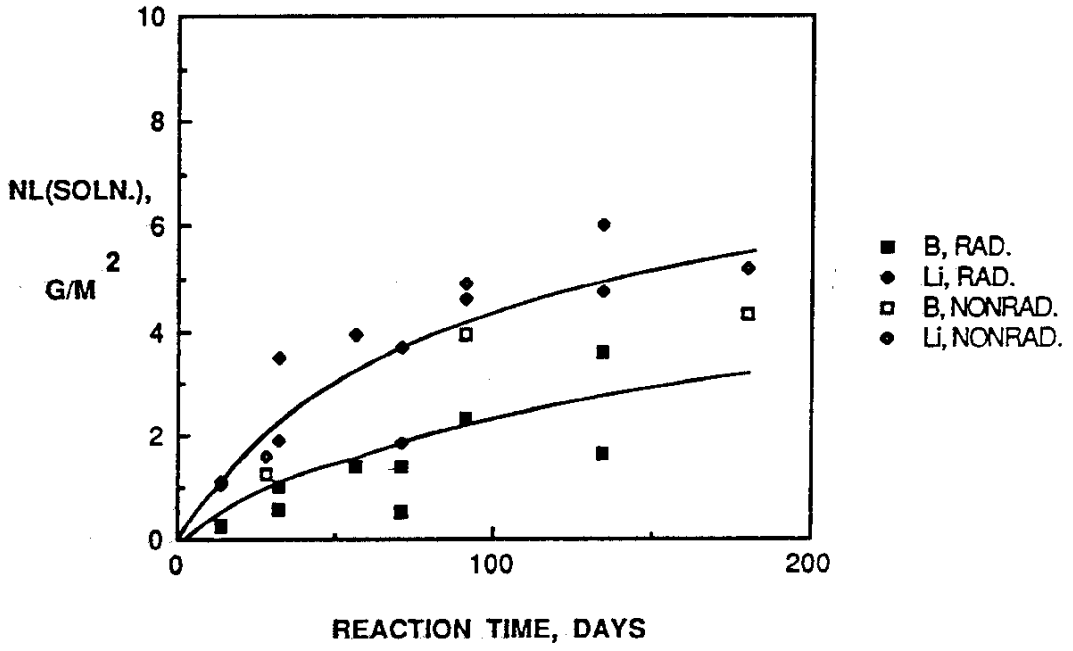

FIGURE 3. Leaching B and Li from Radioactive Glass with Actual SRP Waste and Nonradioactive Glass with Simulated Waste. Lines indicate the Trend of the Data. J-13 Water, T = 90°C, SA/V = $100m^{-1}$