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DP-MS-83-138

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A paper proposed for presentation at the
American Ceramic Society Annual Meeting
Pittsburgh, PA
April 29 - May 3, 1984

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INTRODUCTION

The first high-level radioactive waste to be immobilized into borosilicate glass on a production scale in the United States will be the 30 million gallons of defense waste currently stored at the Savannah River Plant in Aiken, South Carolina. An important objective of waste management programs at Savannah River is to characterize, assess, and ultimately, to be able to predict, the long term behavior of SRP waste glass.

In order to achieve the above objective, a multi-component program is in progress at the Savannah River Laboratory (SRL). One component of this program involves "Repository Interaction Tests" and consists of three main parts. First, tests have been performed in the laboratory in which simulated SRP waste glass was leached in conjunction with proposed waste package components. These experiments have provided information on the effects of package components on glass leaching, as well as on problems in testing complete disposal systems. The tests were performed under well-defined and controlled conditions in the laboratory in order to better understand the complex interactions involved.

In a contrasting set of experiments, simulated SRP waste glass has been buried in an underground facility and allowed to interact with groundwater. These experiments are characterized by the variability inherent in the geology and the hydrology, and other burial considerations. The primary materials used in these tests

* The information contained in this article was developed during the course of work under Contract DE-AC09-76SR00001 with the U.S. Department of Energy.

are those of the proposed burial sites. The tests are exemplified by the joint SRL/Swedish program that has been in progress for over one year, involving the burial of over 100 SRP waste glass specimens in the granite Stripa mine in Sweden. This year a new joint effort will begin between SRL and Belgium which will involve burial of SRP waste glass in the clay geology of Mol, Belgium. Later this year, the first in-situ tests to be conducted in the US will begin in the salt site at WIPP and include glass compositions from the United States, Germany, France, Japan, and Canada. In addition, a natural glass composition (basalt) will be studied.

An intermediate series of tests are the repository simulation experiments described in this paper. These tests are designed to assess the performance of SRP waste glass under the most realistic repository conditions that can be obtained in the laboratory. These tests simulate the repository environment as closely as possible and introduce systematically the variability of the geology, groundwater chemistry, and waste package components during the leaching of the waste glass. The tests evaluate waste form performance under site-specific conditions, which differ for each of the geologic repositories under consideration. Data from these experiments will aid in the development of a realistic source term that can describe the release of radionuclides from SRP waste glass as a component of proposed waste packages. Hence, this information can be useful to optimize waste package design for SRP waste glass and to provide data for predicting long-term performance and subsequent conformance to regulations. The repository simulation tests also help to bridge the gap in interpreting results derived from tests performed under the control of the laboratory to the uncertainity and variability of field tests. In these experiments, site-specific repository components and conditions are emphasized and only the site specific materials contact the waste forms. An important feature of these tests is that both actual and simulated waste glasses are tested identically.

SRL/Repository Program Coordination

Three specific geologies have been defined in the US for more detailed examination as potential nuclear waste repositories. Savannah River Laboratory has entered into joint programs with each of these repository developers. This includes studies of SRP waste glass leaching in the presence of tuff from Nevada (LLNL/SRL), basalt from the state of Washington (BWIP/SRL), and salt formations from several possible states (ONWI/SRL). These site specific tests will assess the effects of the specific geology, hydrology, and package components considered on the leaching behavior of SRP waste glass. The participants involved, the site specific repository conditions used for each set of system tests, and the overall division of responsibilities are summarized in Tables 1 and 2 and Figure 1, respectively.

Repository Simulation Tests

Important features of the "Repository Simulation Tests" include the following: (a) the primary leaching vessel is the host rock, as in the repository borehole; (b) actual groundwater is used as leachant (as in the tuff experiments) or where this is not available, a simulated groundwater composition as complete as possible is substituted; (c) a relatively high and more realistic ratio of surface area of glass to volume of leachant (SA/V) is emphasized; (d) package components are introduced into the rock leaching vessel individually; (e) an outer Teflon® vessel surrounds the rock cup and contains groundwater for internal rock calibration; and (f) leaching tests are performed on nonradioactive as well as radioactive waste forms. The test represents a modification of a standard and widely used leaching experiment, MCC-1. In fact, some tests have been performed at an SA/V of 0.1 cm^{-1} to more closely tie these tests back to MCC-1. The apparatus for the current tests is shown schematically in Figure 2. Rock cups for the three geologies now under study and the glass samples used in the experiments are shown in Figure 3 along with the leaching assembly in Figure 4.

The basalt repository simulation test will utilize an additional feature of the basalt repository. This involves the use of anoxic conditions which can be maintained during an entire experiment. Recently we have shown that GR-4 basaltic groundwater can achieve an Eh of -0.33 volts in the laboratory by pre-equilibration with crushed rock in an ultra-pure argon environment. The solution remains anoxic during the 28 days of leaching of the waste glass in basalt rock cups at 90°C. The final Eh after 28 days of leaching in an oven in the argon box was very close to the original value of -0.33 volts. A final Eh of -0.24 volts can also be obtained after leaching in Parr bombs external to the argon box. All samples were loaded and unloaded in the high purity argon environment.

Only the static MCC-1 based test has been performed thus far in the repository simulation program, although the leaching apparatus contains the flexibility to perform other types of experiments as well. In Phase I of this program, the contained vessels are being placed into ovens controlled to ±1°C at 90°C and withdrawn at time intervals of 1, 3, and 6 months. The leachates are analyzed after the tests to determine the species extracted from the waste glass and package components, and these data are then correlated with bulk and surface studies of the leached components. Phase I of the program was started in 1983 and represents a "test-of-the-test". Phase I is providing information not only on the experimental approach used, but also initial data on the importance of site-specific conditions and package components on waste glass performance. Phase II of the program will assess the leaching behavior of the waste forms in the more realistic and complex systems currently under consideration and out to longer time periods. Ultimately, a complete system mass balance will be attempted to quantitatively separate the performance of the waste glass from the influence of each of the package components.

Major Limitations of Repository Simulation Tests

While the performance of waste glass with potential leachants has been extensively studied over recent years, the number of tests performed on entire waste packages is significantly limited. This is due in part to the absence of "standard repository-type experiments" and the complexity of interpreting the many interactions that may be involved. More specifically, the two major limitations and the approaches used in the current program for addressing these limitations are as follows:

1. Determining what fraction of a given species found in solution came from waste glass.

The overall effect of components in solution is first assessed by studying the leaching behavior of each component separately and then various combinations. However, this is not sufficient to quantitatively determine the performance of waste glass in the complete system. It is also necessary to define "unique elements" which come from the waste glass alone. This can be most effectively performed by overlapping studies involving both nonradioactive and radioactive waste glass. For example, lithium is an element in the glass which does not exist in signifcant quantities in most rock or package components now under consideration. Boron is almost as useful because only small amounts are released, or exist in some rock types. In addition, for leaching of radioactive specimens, the radioactive species are specific to the glass composition and therefore, waste glass leaching can be most easily assessed by radiometric techniques. Ultimately, a complete mass balance is necessary to quantitatively assess the effects of waste package components on glass performance.

2. Accounting for the heterogeneity of different rock samples used for each test.

The concentration of species in solution leached from a given type of rock can vary significantly even for rock samples obtained from adjacent positions within a single core. Therefore, leaching of rock from a given batch does not necessarily reflect the contributions made from a specific rock sample used in the test and preleaching or postleaching of the test rocks can't always provide the information needed. For example, preleaching the rock may extract the key elements before the system test can be performed and postleaching the rock may not be informative because the elements of interest may have already been extracted during the test.

The current repository simulation or "rock-cup" experiments attempt to address this problem by using an internal calibration standard. This is achieved by analyzing the annular space between the rock-cup and the outer Teflon® vessel. These concentrations are then calibrated to the final surface area of the rock to groundwater volume [SA(r,o)/V] in this region. The ratio is then normalized to the different final [SA(r,i)/V] inside the rock container. For example, the concentrations of lithium [adjusted for SA(r)/V] measured in solution inside and outside of the first rock-cup (no waste glass or package components) was 0.16 versus 0.11 ppm. For the second rock cup, these amounts were even lower and still consistent at 0.02 versus 0.01 ppm. Therefore, for experiments performed with rock cups alone, this approach has produced very similar concentrations of key elements inside and outside the rock container. While the approach of adjusting the amount of species inside the rock by that found in the annular space looks promising, it must be noted that the amount of tests completed thus far is limited and more data are needed to fully assess the applicability of the internal calibration method.

Preliminary Data

The experimental portion of Phase I of the tuff program has recently been completed. In Table 3, pH changes for the nonradioactive tests is summarized. Note the variation that can exist in two rock cups are represented by the final pH values obtained after six months of leaching of rock alone (a similar variation has been observed in scouting tests using basalt). An important point is represented in the table by the final pH values obtained after leaching of glass by itself versus leaching of the glass in the presence of the system. The final pH of glass alone after leaching at 90°C for six months and at a SA/V of 1.0 (cm^{-1}) is about 10, compared to the significantly lower pH value of about 8.5 for leaching of glass in the system. This suggests that the glass may be leaching less while in the system. The beneficial effect(s) of the system are reflected in the lower, less aggressive, final pH, which is primarily a result of buffering effects provided by the rock. Independent of a possible reduction in waste form leaching, the absorption of species of interest on surfaces of rock and package components would be expected to be the most significant effect reducing the amount of species found in solution.

In Figures 5 and 6, the normalized elemental mass loss for lithium and boron are summarized for leaching of glass alone compared to leaching of glass in a system composed of tuff rock and 304 L stainless steel canister material. The system data are depicted assuming that there is no transfer of groundwater from inside the rock to outside and also depicted assuming that all the elements of interest inside and outside the rock is derived from the glass. As shown in the data, less lithium and boron appear in solution after the waste glass is leached in the presence of the rock compared to leaching in the absence of the rock. In Figure 7, a comparison is made for the amount of lithium found in solution after leaching of simulated versus radioactive waste glass. These data indicate that the glasses leach similarly. The relatively small differences in the amount of lithium in solution for these two tests can be primarily attributed to differences in composition between the simulated and radioactive glasses. When correlation of the nonradioactive and radioactive data is completed and a mass balance is performed, the actual release rates obtained from the waste glass within the system and each of its components will be determined.

An important assumption of being able to use the advantages of both nonradioactive and radioactive systems is that they perform similarly with respect to key elements. This assumption is supported by data obtained from the current nonradioactive and radioactive system (Figure 7).

Future Work

Scouting tests on tuff and basalt systems are completed and tests involving salt are currently in progress. Phase I of the tuff program, involving leaching tests out to six months in duration, has been completed for the simulated waste glass tests and partially completed for the radioactive studies. Analyses of the large amount of data produced are still in progress. A complete mass balance will be attempted as more data become available. Phase I of the basalt tests will begin shortly in which anoxic conditions will be used during the leaching experiments. In addition, there will be an exchange of simulated waste glass, salt, and package components with HMI of West Germany who will also be performing tests similar to the SRL tests involving salt. This will allow a more extensive matrix to be investigated in the salt programs and an independent check of the experimental procedures to be performed.

TABLE 1

Repository Simulation Studies

	REPOSITORY DEVELOPERS
Tuff	• NNWSI [Nevada Nuclear Waste Storage Investigation] Lawrence Livermore National Laboratory
Basalt	• BWIP [Basalt Waste Isolation Project] Rockwell Hanford Project
Salt	• ONWI [Office of Nuclear Waste Isolation]

TABLE 2

Repository Simulation Test Conditions

	TUFF	BASALT	SALT
TIME	←	1 mo., 3 mo., & 6 mo.	→
TEMP.	←	90° C	→
SA/V	←	[0.1] 1.0 cm^{-1}	→
P	←	1 atm.	→
FLOW	←	Static	→
CANISTER	304L SS	304L SS	304L SS
OVERPACK	None	Carbon Steel	Carbon Steel
LEACHANT	J-13	GR-4	WIPP A Permian Brine
SIMULATED WG	←	165/TDS [Cs, Sr, U]	→
RADIOACTIVE WG	←	165/Tank 42	→
BACKFILL	←	Defined in Phase II	→
Eh	Oxidizing	Reducing	Neutral

TABLE 3

Tuff Tests - Phase 1

Time	Glass Only		Tuff Only	Tuff+Glass	Tuff+Glass +304L SS	
SA/V[cm-1]:	1.0	.1	1.0	1.0	1.0	.1
1 mo.	[9.30]		[7.35]	[7.60]	[8.54]	[8.37]
	[9.15]		[7.35]	[8.08]*	[8.49]	[8.37]
3 mo.	[9.59]			[8.34]	[8.23]	
	[9.70]			[8.29]*	[8.22]	
6 mo.	[10.18]	[9.76]	[7.31]	[7.73]	[8.43]	
	[9.87]		[8.48]	[8.53]*	[8.80]	

Initial pH of J-13 GW= 7.35

* Denotes Pt baskets

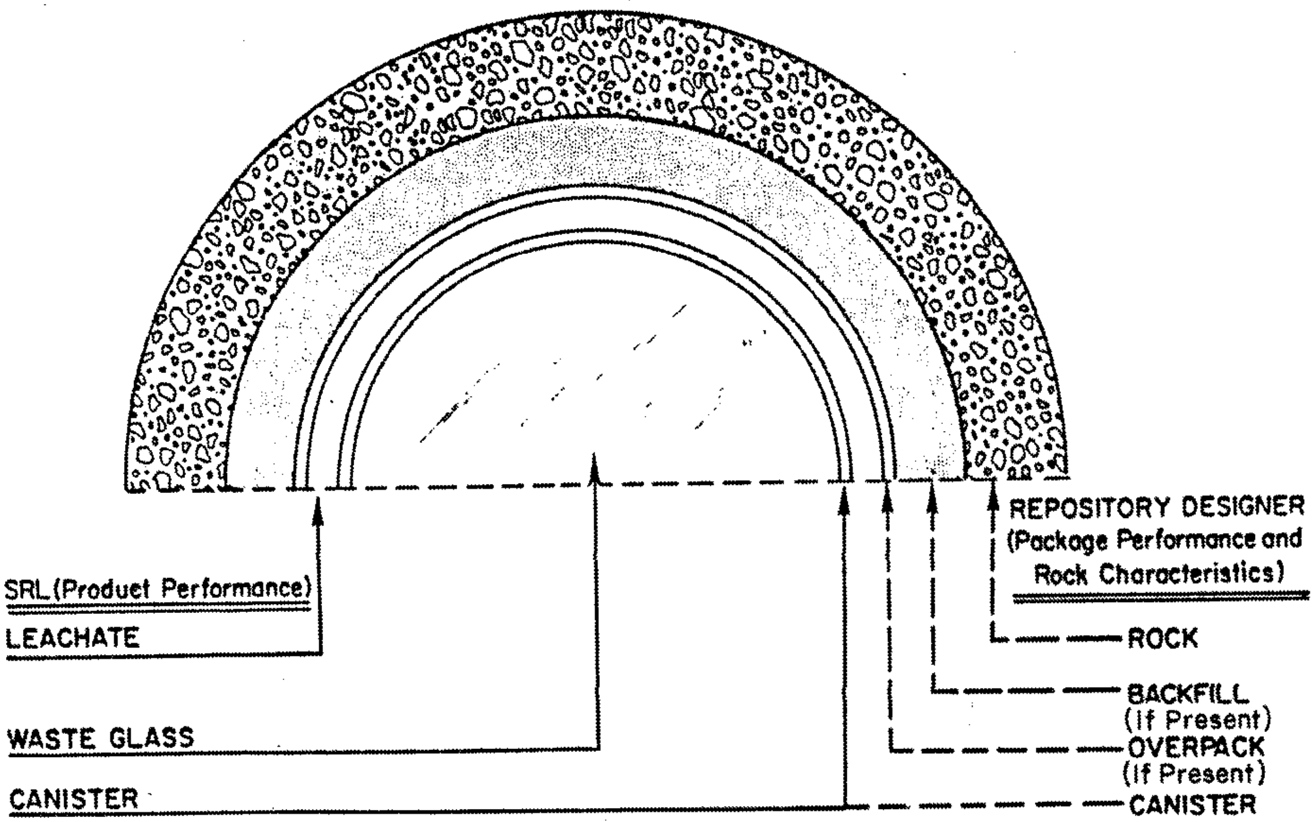

FIGURE 1. Analyses and Responsibilities

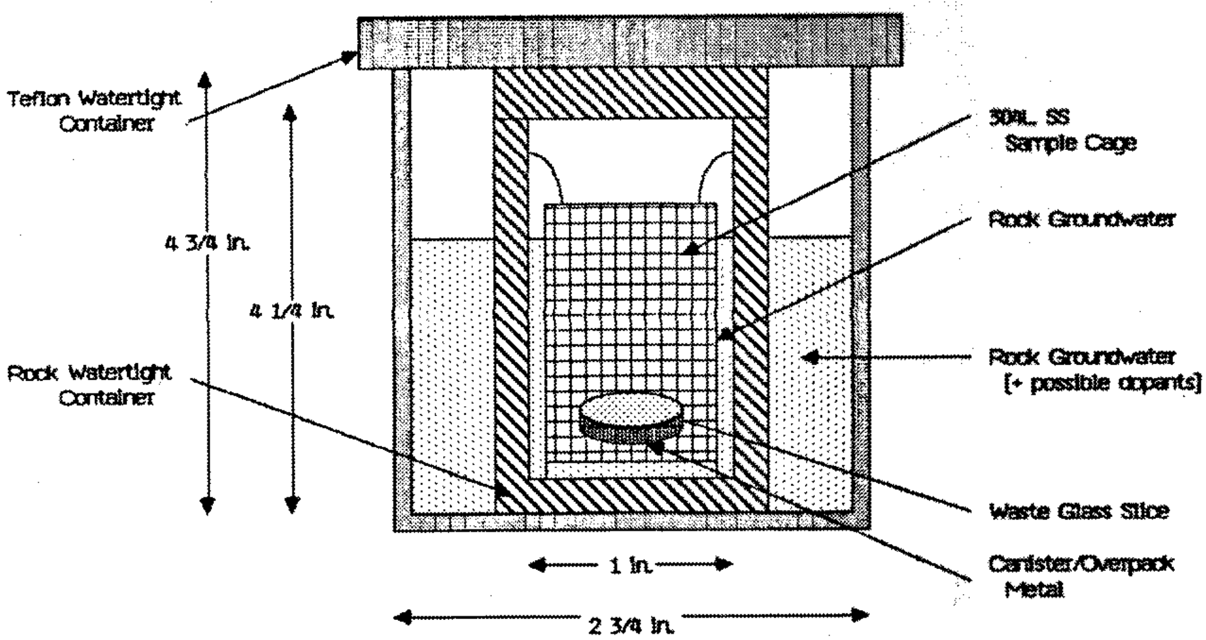

FIGURE 2. Experimental Apparatus

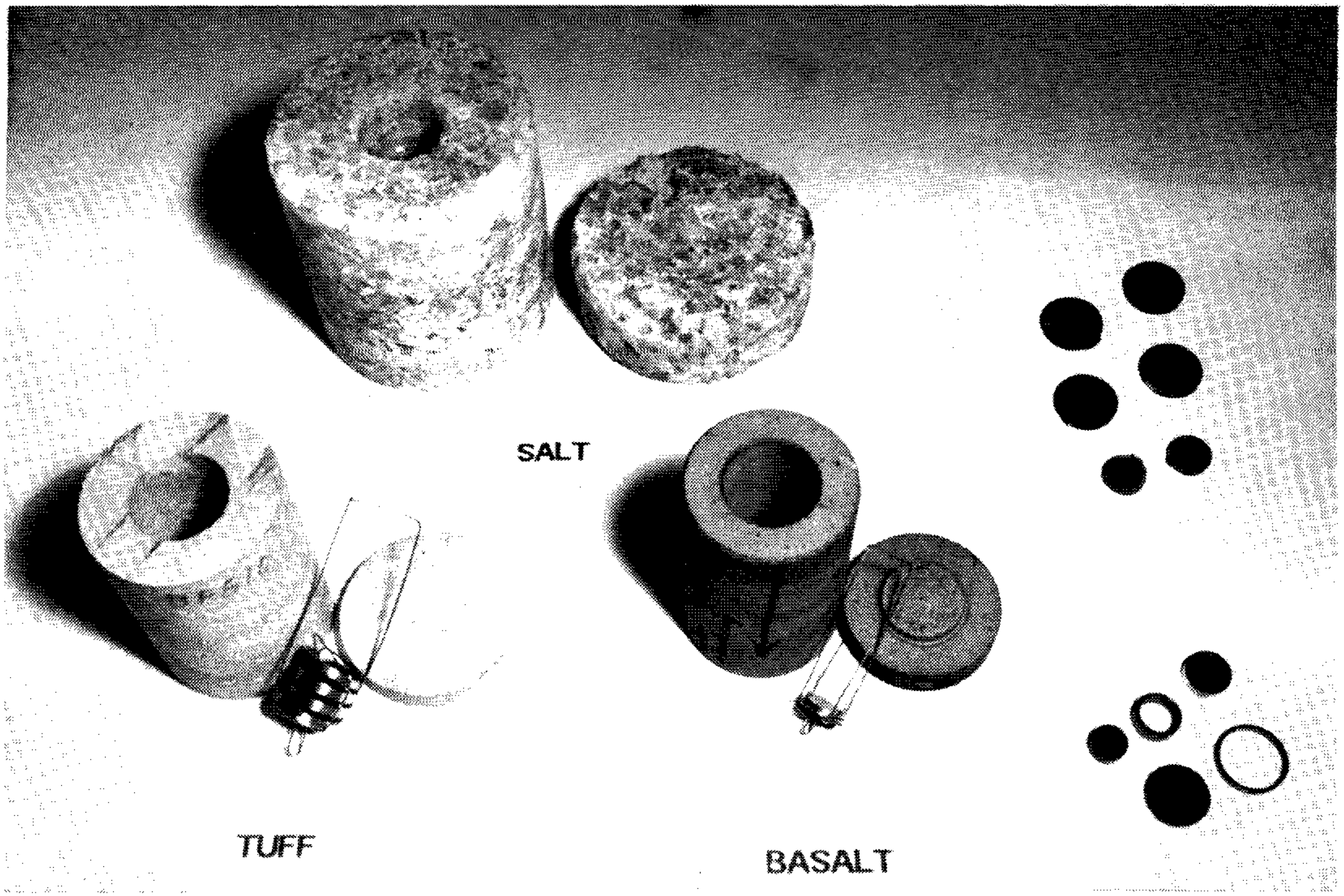

FIGURE 3. Rock Cups and Waste Glass Samples

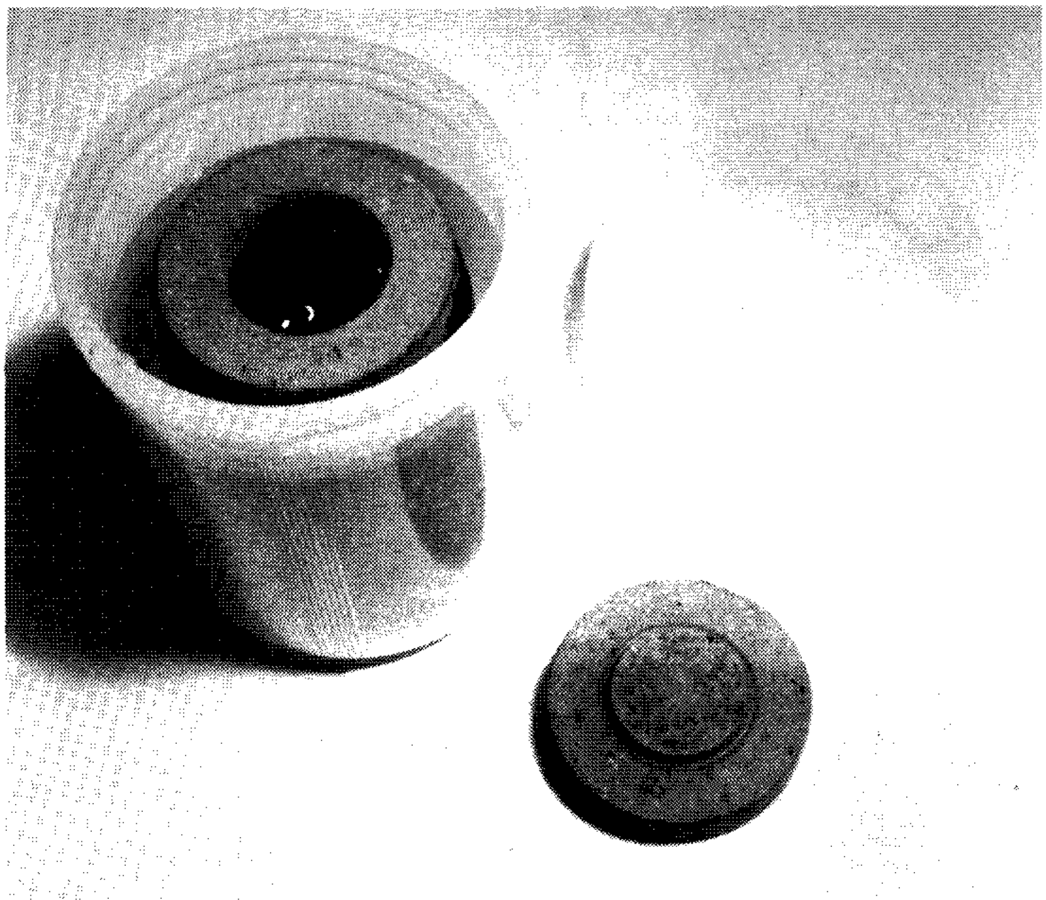

FIGURE 4. Experimental Unit

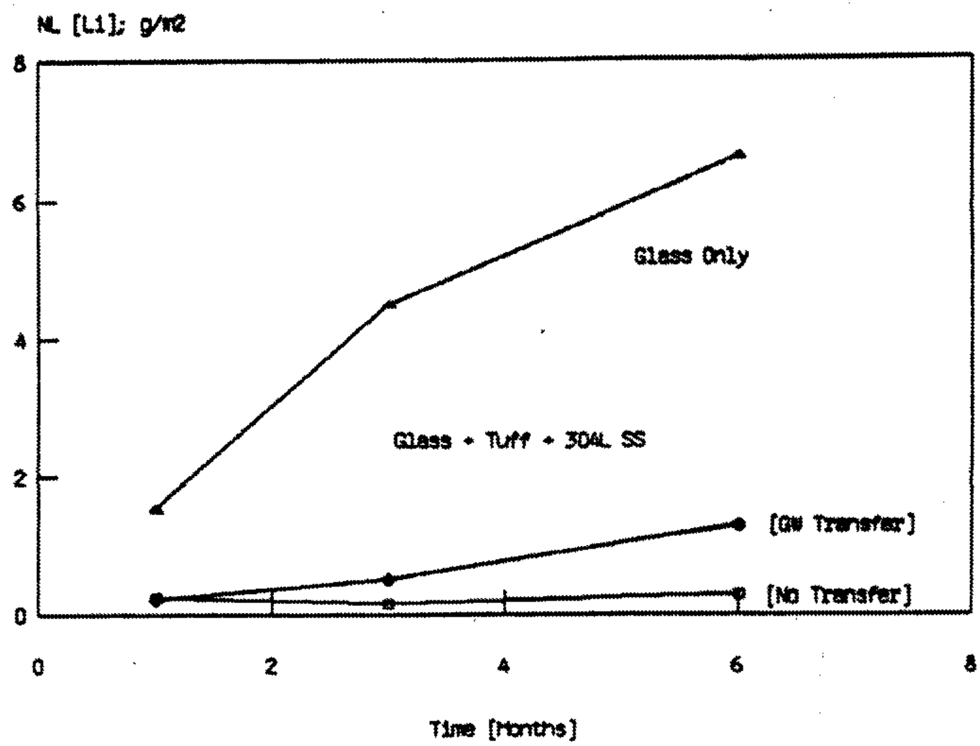

FIGURE 5. NL of Lithium in J-13 Tuff GW and System

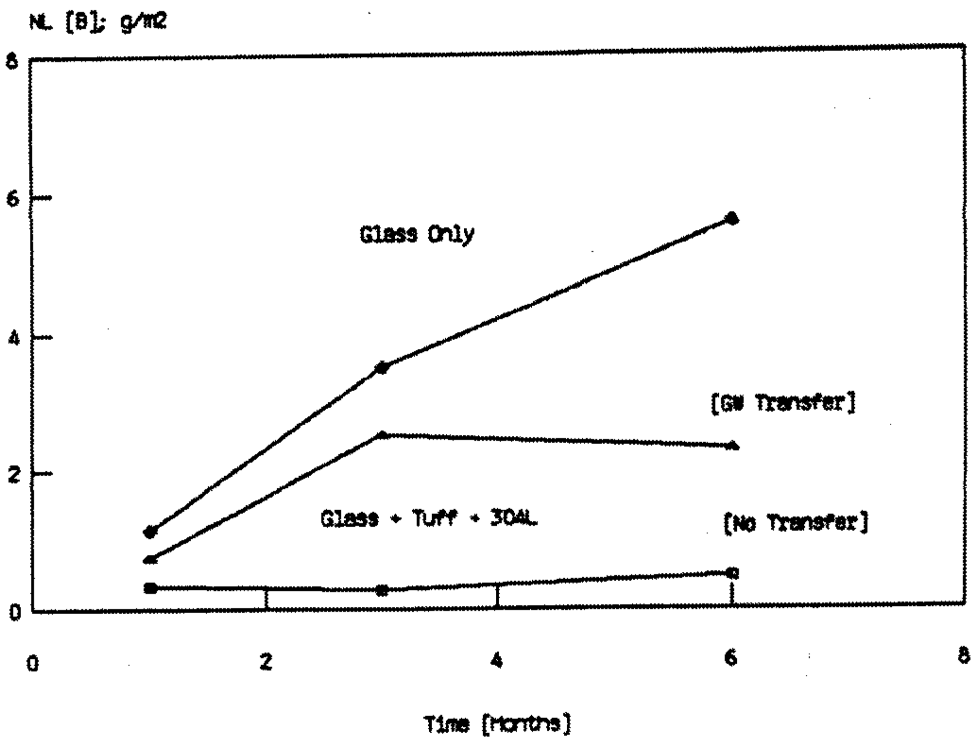

FIGURE 6. NL of Boron in J-13 Tuff GW and System

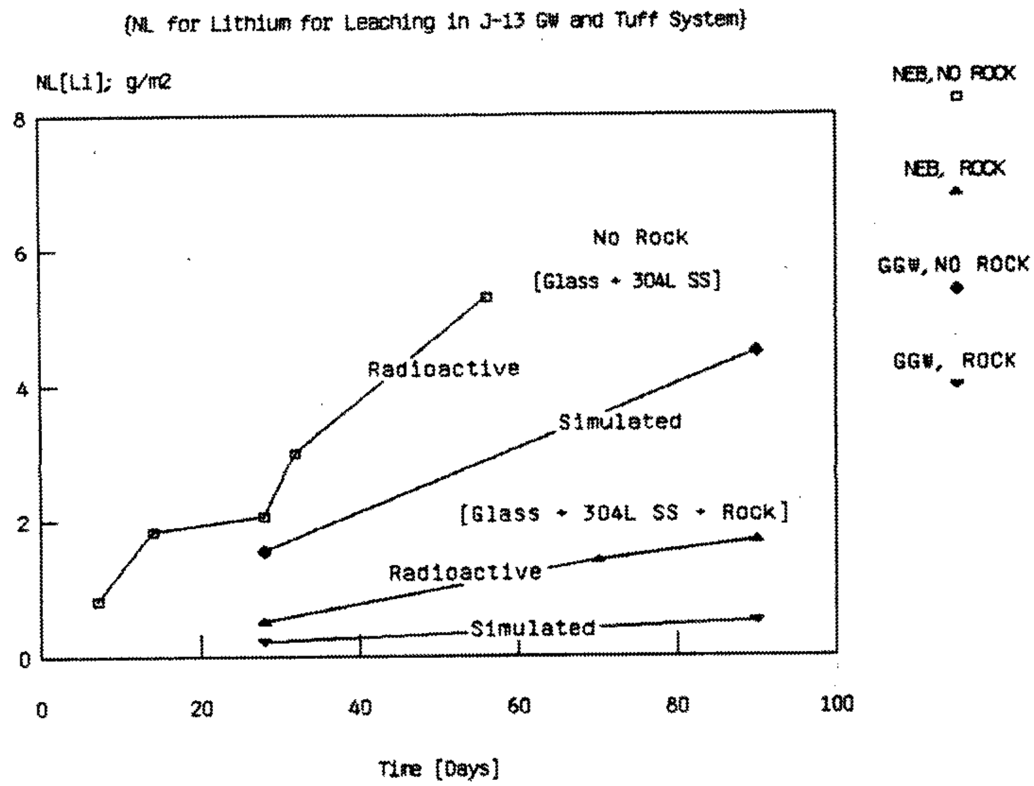

FIGURE 7. NL (Li) for Radioactive versus Non-Radioactive Tests (J-13 Tuff GW and System)