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SINGLE-PASS CONTINUOUS-FLOW LEACH TEST OF PNL 76-68 GLASS: SOME SELECTED BEAD LEACH I RESULTS

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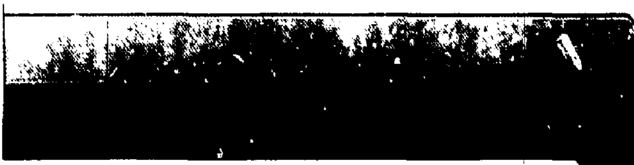

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SINGLE-PASS CONTINUOUS-FLOW LEACH TEST OF PNL 76-68 GLASS: SOME SELECTED BEAD LEACH 1 RESULTS

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ABSTRACT

A single-pass continuous-flow leach test of PNL 76-68 glass beads (7 mm dia) was concluded after 420 days of uninterrupted operation. Variables included in the experimental matrix were flow-rate, leachant composition, and temperature. Analysis was conducted on all leachate samples for ^{237}Np and ^{239}Pu as well as a number of nonradioactive elements. Results indicated that flow-rate and leachant systematically affected the leach rate, but only slightly. Temperature effects were significant. Plutonium leach rate was lower at higher temperature suggesting that Pu sorption onto the beads was enhanced at the higher temperature. The range of leach rates for all analyzed elements (except Pu), at both temperatures, at all three flow rates, and with all three leachant compositions varied over only three orders of magnitude. The range of variables used in this experiment covered those expected in many proposed repository environments. The preliminary interpretation of the results also indicated that matrix dissolution may be the dominant leaching mechanism, at least for Np in bicarbonate leachant. Regardless of the leaching mechanism the importance of this study is that it bounds the effects of repository environments when the ground water is oxidizing and when it doesn't reach the waste form until the waste has cooled to ambient rock temperature.

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INTRODUCTION

Ground water leaching of radioactivity from the waste form, with subsequent transport to the biosphere, is the primary hazard to mankind from the geological disposal of nuclear wastes. A safety assessment for a nuclear waste repository requires an understanding of its response to invading ground water. Laboratory leaching studies provide insight to the leaching phenomenon. The minimum information required for a safety assessment is the rate at which radioactivity is released from the waste form to the ground water. However, the extrapolation of release rates based on short term laboratory studies to those expected after 10^5 to 10^6 years is dubious. In order to better extrapolate these leach rates, the mechanisms of leaching must be understood. Moreover, the laboratory experiments must be conducted under conditions which simulate the repository environment as closely as possible.

The objectives of Bead Leach I were twofold. First, a comparison was done on the leaching of PNL 76-68 borosilicate glass beads (~ 7 mm dia) using a modified IAEA leach procedure (Bradley, et al., 1979) and the LLNL single-pass continous-flow (SPCF) leach procedure (Coles, 1980). The modified IAEA test was done at Battelle-PNL on the same glass using the same leachant compositions as the LLNL SPCF test and at the common temperature of 25°C. The second objective was to test the affects of various parameters on the leach rate. Temperature, flow rate, and leachant compositions were varied over the ranges of values expected in a geological repository after the waste had thermally cooled to ambient rock temperatures. This was an attempt to bound the leach rate for this glass under a variety of repository relevant conditions.

EXPERIMENTAL

The LLNL SPCF leach test has been described in detail elsewhere (Weed and Jackson, 1979, Coles and Bazan, 1980, Coles, 1979, Coles, et al., 1979). It is a system where the leachant flows through a cell, interacts with the waste form, and the resultant leachate is collected and analyzed. The advantage of this system is that it simulates the conditions of a flooded repository where ground water flows through a natural aquifer. Flow rates can be adjusted to the low linear flow rate of 0.72 m/year. Typical ground water velocities can vary from 1.5 m/y to values in excess of 500 m/y (Todd, 1959). Clearly, a repository would be located in an environment with the lowest possible ground water flow rate.

For this first bead leach experiment, we selected flow rates which were experimentally practical and were in the high flow-rate end of the natural range. This allowed us to look at a worse case situation for repository siting as well as investigate the effect of flow rate on leach rate. Figure 1 is a schematic of the experimental design for the Bead Leach I experiment. Flow rates were 7, 30, and 220 m/y.

Other variables in this experiment are shown on Figure 1. Two temperatures (25°C and 75°C) and three leachant compositions (distilled water, 0.03N $NaHCO_3$ water, and saturated salt brine) were utilized in a partially replicated experiment. Replication (as triplicates) were done for the 25°C, 30 m/y flow rate channels.

This experiment was run continuously for 420 days and one day samples were collected on days 1, 2, 3, 6, 11, 20, 38, 70, 120, 230, and 420. Aliquots from these samples were radiochemically purified (Rego, 1979) and counted on an α-spectrometer for analysis of ^{237}Np and ^{239}Pu. Other aliquots were analyzed by inductively-coupled plasma-optical emission spectroscopy (ICP) for B, Cd, Fe, Mo, Ni, Si, Sr, Ti, U, Zn, Ca, and Na. Some selected samples were also analyzed by x-ray fluorescence (XRF) for Mo, U, Ca, Cs, Ba, and Zr. Only the ^{238}U, ^{237}Np, and ^{239}Pu were radioactive. All other elements were either mock fission products or glass matrix elements. Also, the pH, Eh, and conductivity of the leachates were measured and the variations in the flow rates of each channel was monitored throughout the experiment. A more complete description of the experiment and results can be found in another report (Coles, 1981).

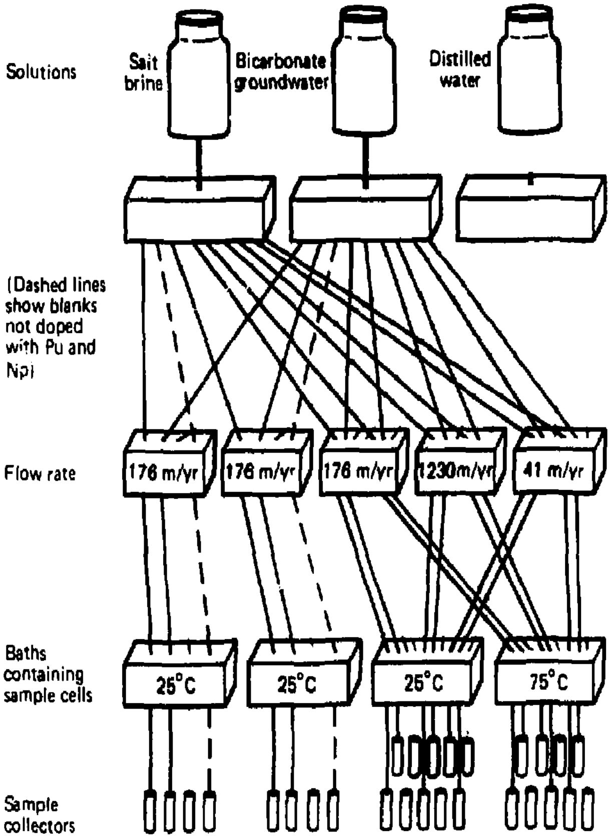

FIGURE 1. Experimental design for the Bead Leach I experiment. This experiment was a partially replicated study of PNL 76-68 glass beads using the SPCF leach test.

RESULTS

The effect of leaching method, temperature, flow rate, and leachant composition will be discussed in order.

LEACHING METHOD EFFECTS

Figure 2 presents the Np leach rate data for PNL 76-68 glass beads leached with 0.03N $NaHCO_3$ leachant. The log of the leach rate (as g glass leached/cm^2 · day, based on ^{239}Np release) is plotted against the log of time (in days). Solid lines are the SPCF leach rate data at 25°C. The three upper lines with the F, M, and S symbols (fast, medium, and slow flow rates; these are 7, 30, and 220 m/y respectively) are the SPCF leach rate data at 75°C. The open circles are Battelle-PNL leaching data obtained at 25°C using a modified IAEA procedure. Battelle-PNL did not do any leach tests at 75°C. Clearly, the LLNL and PNL data show excellent agreement at 25°C, regardless of the fact that two separate laboratories conducted these experiments using different leaching techniques.

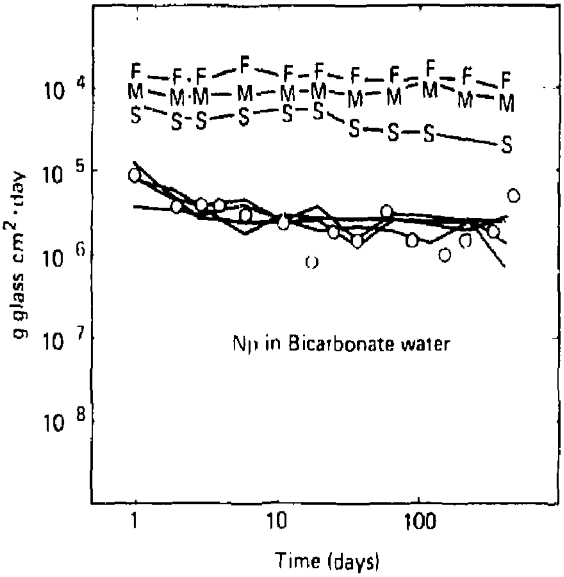

FIGURE 2. Leach rate data of PNL 76-68 glass beads. The leachant was 0.03N $NaHCO_3$ water. Clustered solid lines are the 25°C data. Data with F,M,S symbols are the 75°C data at fast, medium, and slow rates respectively. The open circles are Battelle PNL data at 25°C using a modified IAEA leach test.

TEMPERATURE EFFECTS

Figure 2 shows the temperature effects on Np leach rate in 0.03N $NaHCO_3$ leachant. The 75°C channels (F, M, S symbols) show about an order of magnitude higher leach rate than the 25°C channels. Also, flow rate effects can be resolved at 75°C but cannot be resolved at 25°C. The leach rate data at 75°C tends to vary less with time than the 25°C data. The 25°C data appears to decreases more with time.

Although not shown in Figure 2, the Pu leach rate behavior was peculiar at 75°C. While the same flow rate effect was observed, the 75°C data was about an order of magnitude lower than the 25°C data. This might indicate that Pu resorbs onto the bead-surface silica-gel layer more readily at the higher temperature. Certainly, Pu is less soluble at 75°C than it is at 25°C. A. Friedma at ANL has recently observed the build-up of Pu on the surface of leached glass.

FLOW-RATE EFFECTS

Flow rate effects (see Figure 2) were observed for the higher temperature channels only. For all elements and radionuclides analyzed, the leaching rate and flow rate are consistantly correlated, although the effect is small. Higher flow rates give higher leaching rates. Figure 3 is a graph of the leach rate for Np in 0.03N $NaHCO_3$ leachant at 75°C plotted against volume flow rate. These data are for day 420, which was the last sample in the experiment. At low flow rates the leach rate increases with flow rate indicating that reduced chemical potentials can occur as leached constituents build up in the solution. With increasing flow rate, this effect decreases as the leached constituents are flushed from the cell. Since the leach rates are calculated on the basis of initial sample mass and area, the day 420 rates are actually lower limits for the true leach rate. Nonetheless, the qualitative indication that increased flow rates do not proportionately increase leach rates is almost certainly correct.

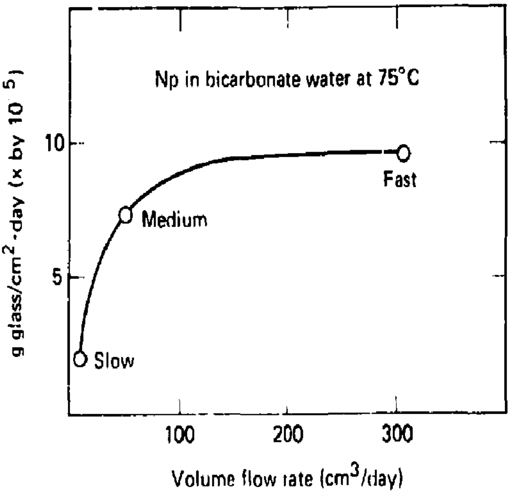

FIGURE 3. Effect of flow rate on leach rate for Np at 75°C. The leachant was 0.03N $NaHCO_3$ and the data shown is for the 420th leaching day. These data are from the Bead Leach I experiment.

LEACHANT COMPOSITION EFFECTS

Three leachants were used in the Bead Leach I experiment. A saturated salt brine was used to simulate the effects of waste in a salt repository. A 0.03N $NaHCO_3$ leachant was used to simulate typical $NaHCO_3$ ground waters. Distilled water was used as a baseline for comparison to the other leachants. Figure 4 presents the leaching data for Np at both 75°C and 25°C for all three leachants for the full 420 day experiment. Very little difference in leach rate occurs from using these three different leachants. The $NaHCO_3$ leachant shows a slightly higher leach rate at both temperatures. Except for the first week of leaching, the brine shows intermediate leaching rate and the distilled water the lowest leaching rate at both temperatures. The 75°C data were for the single, medium flow-rate channels only (30 m/y). The 25°C data are for triplicated channels at medium flow rate and single channels for the other flow rates. As mentioned previously, since flow rate effects were not resolved at 25°C, a plot of all 25°C data has been simplified to a zone. All data scatter for these various channels fall within the zones indicated for each leachant. Regardless of the overlap of the three zones, the subtle differences in leachant effect is consistant with that observed at 75°C. It is also important to point out that the pH value for the three leachants are 9, 7, and 6 for the $NaHCO_3$, brine, and distilled water respectively. Thus the leach rate effect may be more controlled by pH than by the specific chemical composition of the leachant.

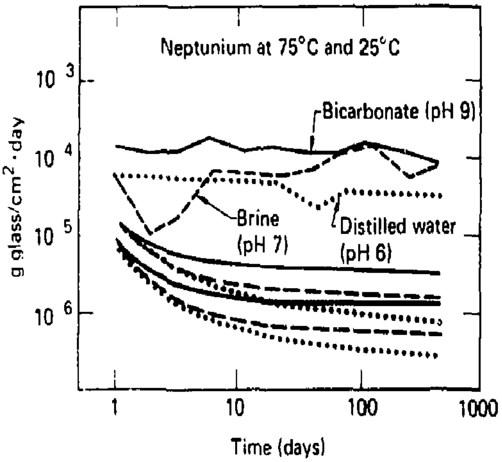

FIGURE 4. Effect of leachant on leach rate for NP. Upper single lines are the 75°C data. Lower zones are the 25°C data. These data are from the Bead Leach I experiment.

IMPLICATIONS FOR MECHANISMS

For this prelimary report on the Bead Leach I leaching experiment, we have begun to investigate the mechanisms for glass leaching using the SPCF leach method. A simplified leaching model has been proposed to explain the behavior of glass in contact with an aqueous solution (Clark et al., 1979). The scheme proposed is an initially diffusion-controlled reaction followed by glass matrix dissolution. The diffusion of elements from glass is related to the square root of time and glass dissolution is linearly related to time by the equation:

$$Q = at^{1/2} + bt \qquad (1)$$

where Q is the quantity of glass leached, t is the time and a and b are the appropriate constants.

To test whether either of these simplified mechanisms applies to our leaching data, we plotted the cumulative fraction of glass leached (CFL) as a function of both t and $t^{1/2}$. A straight line for the CFL vs t graph indicates glass dissolution is the dominant leaching mechanism. A straight line for the CFL vs $t^{1/2}$ graph indicates elemental diffusion through the glass is the dominant leaching mechanism.

Figure 5 is a plot of the Np leaching data at 25°C, medium flow, and with the bicarbonate leachant plotted against both t and $t^{1/2}$. Error bars are the standard deviation from the mean of the three replicate channels. Clearly, no straight line relationship exists for CFL when plotted against $t^{1/2}$. However, when CFL is plotted against t, a straight line results. This indicates that for Np, under the conditions specified, glass dissolution seems to be the dominant leaching mechanism.

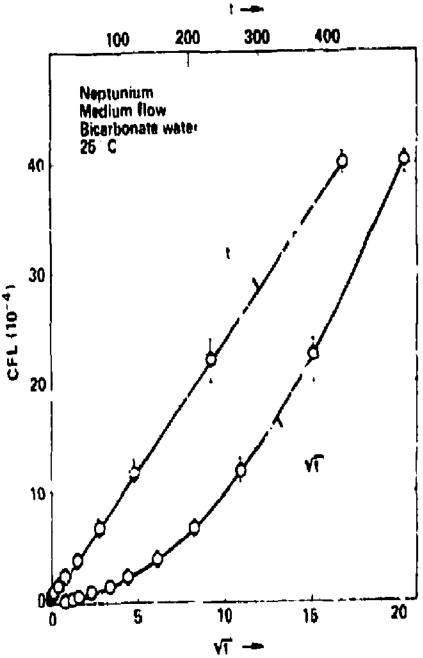

FIGURE 5. Cumulative fraction of glass leached, based on Np and plotted against days and (days)$^{1/2}$. The flow rate was 30 m/y, the leachant was 0.03N $NaHCO_3$, and the temperature was 25°C. Errors are the standard deviation from the mean of three replicate samples.

Figure 6 is a plot of CFL for Np at 75°C and with $NaHCO_3$ leachant at three flow rates. The data from Figure 5 is also plotted on Figure 6 (dotted line near time axis) for scale comparison. At 75°C, neither plot is linear although the CFL vs t plot is nearly linear for the first half of the experiment. We are continuing to interpret these data as well as the leaching data for all the other elements analyzed. A single, simplistic leaching mechanism will very likely be unable to describe the leaching behavior of PNL 76-68 glass.

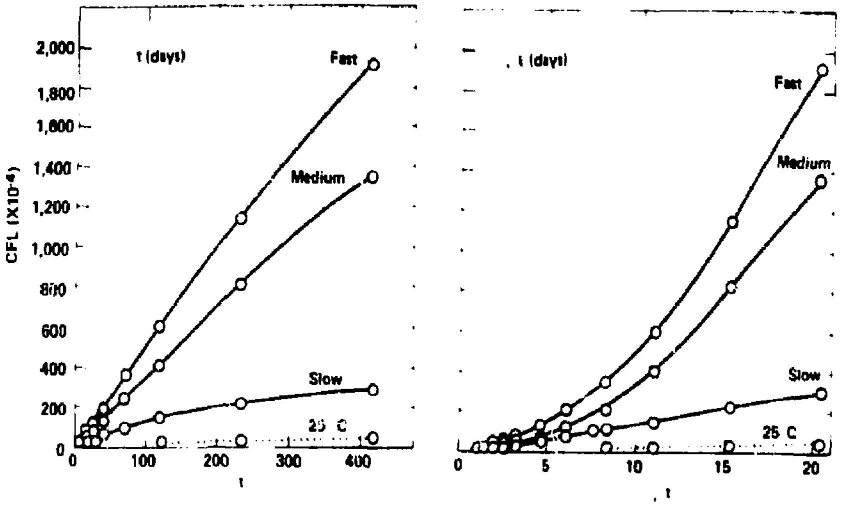

FIGURE 6. Cumulative fraction of glass leached, based on Np and plotted against days and (days)$^{1/2}$. Temperature was 75°C and leachant was 0.03N $NaHCO_3$. Fast, medium, and slow refer to flow rates.

CONCLUSIONS

Temperature shows the most dramatic effect on leach rate for PNL 76-68 glass compared to the other parameters investigated. Leach rate increases with flow rate at 75°C but no flow rate effect can be observed at 25°C. The leachant composition only slightly affects the leach rate at both temperatures. The leach rate increases in the order $NaHCO_3$ > brine > distilled water. It is also important to note that the pH of these three solutions, $NaHCO_3$, brine, and distilled water are 9, 7, and 6 respectively. This may be the controlling factor for the leachant effect. The agreement between PNL's modified IAEA and this study is excellent.

The leaching mechanism for PNL 76-68 glass under flow conditions does not appear to fit the simple diffusion/dissolution model-at least for Np. There are some indications that glass dissolution may be a dominant mechanism at 25°C and probably at 75°C. It can probably be concluded that a model which describes the leaching behavior of this glass will be more complicated than the diffusion/dissolution model which we used for this report.

Probably the most important conclusion to be made from this study is the degree to which the many variables included affect the leaching rate of this glass. The variables studied covered the extreme range of conditions expected in a variety of repositories assuming mildly oxidizing ground water and assuming that the waste had cooled to ambient rock temperatures before being contacted by the ground water. Figure 7 is a simplified plot of <u>all</u> the data obtained for this experiment, except the anolomous Pu data. The leach rate data for these elements, at both temperatures, with all three leachants, and with all three flow rates are plotted against time on this one graph. It can be seen that regardless of the parameters studied, all the resultant leaching rates vary by only three orders of magnitude. The results from this Bead Leach I experiment has essentially bounded the values for leaching rates expected from the repository environments being considered for waste disposal.

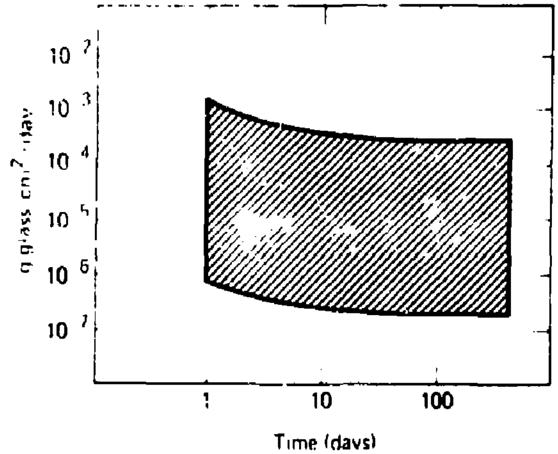

FIGURE 7. A plot of all data (except Pu) from the Bead Leach I experiment. This figure shows that the leach rate of all elements analyzed for and at all flow rates, temperatures, and leachants are located within the lined area.

ACKNOWLEDGMENTS

This complicated experiment was successful due to the combined efforts of many people. H. Weed helped plan, prepare and carry-out the experiment. J. Rego performed the analyses for ^{237}Np and ^{239}Pu, and wrote the computer data-base program. J. Schweiger maintained the experiment for its duration. R. Mensing designed the experiment and performed the statistical analyses. F. Bazan was involved in running the experiment in its later stages and performed the XRF analyses. A. Langhorst performed all ICP analyses. The author wishes to thank the PNL WRIT project for support, L. Ramspott and F. Bazan for reviewing the manuscript, and P. Beringer for typing the manuscript.

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