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CHEMICAL DURABILITY OF ZINC BOROSILICATE NUCLEAR WASTE GLASS

MASTER

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Chemical durability is of primary concern when evaluating the safety of waste glass. For this reason, testing the leachability of the waste glasses is a fundamental part of their development and characterization. The leachability must be understood in terms of the potential thermal and radiation history of the waste glass, and the conditions of possible contact with water. Leachability is also very much a function of glass composition as previously discussed by Wayne Ross.(1) Today, I will limit most of my discussion to one representative waste glass composition, a high-zinc borosilicate formulation which has been studied in detail at Battelle Pacific Northwest Laboratories.

WASTE GLASS COMPOSITION

The composition of the high-zinc waste glass is shown in Table 1. In processing, the glass is formulated by combining a glass frit, shown in the right hand column, with the waste which has been converted to a fine oxide powder in a calciner. For the high-zinc glass, the frit is nominally fed at a gravimetric feed rate 2.8 times that of the calcine, i.e., the glass is 2.8 parts frit and 1 part calcine. In this case, the calcine is assumed to come from a "clean" waste so the fission product loading in the glass is quite high, 23%.

Since in the engineering equipment, the glass is formulated by combining two streams, it is important that flexibility exists, i.e., that fluctuations in the flow rates of the two streams can be accommodated without adversely affecting the quality of the glass. The leachability of waste glasses prepared from a range of frit-to-calcine ratios is shown in Figure 1. The nominal glass composition contains about 26.5 wt% calcine. It is apparent that wide deviations from this ratio can occur without changing the leachability of the product glass significantly.

CONDITIONS OF POSSIBLE CONTACT WITH WATER

The data in Figure 1 were obtained by means of the Soxhlet test. In this test, -45 +60 mesh granules of the glass are exposed to continuously replenished distilled water at approximately 99°C. The apparatus is shown in Figure 2. This test uses high temperature to get data rapidly. It is used mainly as an accelerated test for scouting or screening purposes.

But what are the conditions that might really exist in the unlikely event that the waste glass is exposed to water, and how well do existing tests obtain data concerning these conditions? Three different situations can be envisioned in which water could contact the glass. The first is during water basin storage of waste glass canisters. This essentially is an in-plant process problem; it would not result in release of activity to the biosphere. The water would be very pure at a temperature of 50-60°C. The second case is a cataclysmic transportation accident near a stream or lake. There the water composition would be dependent on the location and the temperature would be ambient. The final case is that of geologic disposal. Here the water composition is also dependent on the geologic location selected. The geologic disposal sites will be carefully selected to assure long term stability. Leaching which could result in release to the biosphere should only occur in the remote future, long after self-heating is no longer a factor. Thus the temperature should again be 50 to 60°C.

Review of the above situations show that low temperatures predominate. For this reason, the standard leach test proposed by the International Atomic Energy Agency (IAEA) is carried out at room temperature. At PNL the test is conducted using the apparatus shown in Figure 3. It is a long-term test carried out over a period of many weeks. The leach water can be either deionized water to obtain baseline data, or water designed to simulate a specific location. The leach water is changed periodically to maximize the leach rate. Figure 4 illustrates this effect. The dynamic system in which the leachant is changed has a higher cumulative penetration than the static system where the glass remains in contact with the same solution throughout the test.

Much of the data in this paper were obtained using the IAEA procedure or slight modifications thereof.

RADIATION EFFECTS

The unique features of waste glass are the high radiation bombardment the glass will receive and the self-heating thermal effects, also due to the contained radioactivity. I will discuss the radiation bombardment and thermal effects separately.

The waste glass will receive high doses of beta, gamma, neutron and alpha radiation. Calculations show that the latter, particularly the alpha recoil atom associated with each alpha event, has the greatest potential to cause deleterious effects in the waste glass. Because of the unique importance of alpha radiation and the very long half lives of many of the alpha-emitting isotopes in waste glass, special accelerated tests are being made using curium-244. Curium-244 has a half-life of only 18 years, thus by using higher concentrations of curium-244 in the glass, it is possible to compress many years alpha dose into only a few months. We have already simulated several thousand years of waste glass alpha radiation and found no significant radiation damage.

Leach rates of high-zinc borosilicate glass containing 1 wt% curium-244 are shown in Figure 5. At the end of this test, the glass had received an alpha dose rate equivalent to about 320 years storage at 25°C. Twenty-five degrees is the most severe condition for radiation damage since elevated temperatures tend to anneal most forms of radiation damage. The leach rate of the glass constituents leached at the same rate as did curium. This is not true. There is actually preferential leaching of some waste glass constituents as shown in Figure 6.

The data in Figure 6 show that, as is well known, the alkalis and alkaline earths, leach more readily than higher valence species. Curium behaves as a rare earth and its leach rate is similar to that obtained for rare earths in other tests. The leach rate of plutonium is intermediate between that of cesium and strontium and that of curium.

The data in Figure 6 were obtained by leaching fully radioactive waste glass. This glass was prepared at PNL by dissolving UO_2 power reactor fuel pellets which had an exposure of over 54,000 MWD/MTU. The uranium and plutonium were removed from the dissolved fuel by counter current solvent extraction, as in an actual reprocessing, to form high-level waste solution. The high-level waste solution was batch calcined and combined with high-zinc borosilicate frit to make full-level radioactive waste glass.

The glass was batch melted in a hot-cell furnace and allowed to cool in the furnace. Microstructural analyses indicate that the glass partially devitrified during the furnace cool-down.

THERMAL EFFECTS

In addition to the direct effects of radiation on the durability of zinc borosilicate waste glasses, the self-heating generated by the radioactive decay may cause changes in the glass structure resulting in changes in the chemical durability of the glass. Given sufficient time and temperature, devitrification and phase separation may occur in the glass. For zinc borosilicate waste glass, these thermal effects can cause leach rates to increase by up to a factor of ten. Figure 7 illustrates this effect for glass stored two months at temperatures ranging from 300 to 900°C. Leach rates were determined using the Soxhlet test. The sample stored at 700°C showed the highest leach rate at 6×10^{-5} grams/cm^2 day. In comparison, the untreated glass had a leach rate of 9×10^{-6} grams/cm^2 day. Similar curves have been observed for glass sorted for one week and one year.

To determine why devitrification increases the glass leachability, samples leached in the Soxhlet apparatus have been examined microscopically. Figure 8 shows before and after photomicrographs of the vitreous glass melted two hours at 1000°C. Before leaching, the glass contains some undissolved precious metals and iron and cerium oxides in an otherwise glassy material. After leaching 72 hours in the Soxhlet apparatus, a thin silica-rich film was observed over the glass. The presence of the film suggests that the glass is being leached by a diffusion mechanism. Fitting long-term leach data to the equation

$$\text{CUMULATIVE PENETRATION} = \text{AX(TIME)}^{\text{B}}$$

lends support to the idea of diffusion as the principle means of leaching the vitreous zinc borosilicate waste glass. The exponent of time was determined to be approximately one-half. For this equation, an exponent of 0.5 indicates diffusion while an exponent of 1.0 indicates corrosion of the glass. Exponents between these extremes indicate a combination of the two mechanisms.

The results of leaching a devitrified piece of glass are shown in Figure 9. Devitrification was induced by storing the glass two months at 700°C. As John Wald described this morning,(2) thermal treatment of zinc borosilicate glass results in microcracking and in the formation of Zn_2SiO_4, $SrMoO_4$, and rare earth silicate phases in the glassy matrix. Leaching appears to remove the molybdate phase as well as the glass matrix itself. The phases remaining have been identified as zinc orthosilicate, the rare earth silicate and the precious metals. Since the glass itself has been removed, a corrosion mechanism appears appropriate for the devitrified glass. Again, long-term leach data lends support to this idea.

LONG-TERM LEACH TESTS

To gain some understanding of the long-term leaching behavior of waste glasses, the IAEA leach procedure is used. Figure 10 shows leach rates through more than a year of testing. As mentioned earlier, the deionized water leachant is changed daily during the first week of the test, weekly for an additional eight weeks, then once a month for six months and finally semiannually. Leach rates are determined by the concentration of individual elements in the leach solution. The graph shows the leach rates for cesium, strontium and uranium. Glass leach rates based on cesium and strontium are constant at approximately 10^{-7} grams/cm^2 day. Leach rates based on uranium are an order of magnitude lower. Similar to the results observed from the Soxhlet leach test, long-term leach rates increase a factor of ten with devitrification.

To make long range estimates of the amount of material leached from zinc borosilicate waste glass, data from the long-term test are expressed as cumulative penetration in centimeters. Figure 11 shows a log-log plot of cumulative penetration as a function of the total time leached. The curves are based on the cesium behavior for the vitreous glass and for glass devitrified two months at 700°C. Since the curves are linear they may be extrapolated to longer time periods to get an indication of the amounts of materials leached.

Based on cesium behavior, devitrified glass would be penetrated one millimeter in 1000 years. The vitreous glass would be penetrated .01 millimeter in 1000 years and one millimeter in 100,000 years. If strontium leach data are used to make the extrapolation, the devitrified glass would be penetrated half a millimeter in 1000 years or a centimeter in 100,000 years. The vitreous glass would be leached .01 millimeter in 1000 years or a millimeter in 100,000 years. In making these extrapolations, it is assumed that the glass will be in continuous contact with the leachant for the entire time of the extrapolation and that the leachant will be flowing past the glass. The amount of material released would be less than predicted if the assumptions do not hold.

SUMMARY

A zinc borosilicate glass has been developed for the solidification of high-level radioactive wastes. The glass can accommodate wide ranges in waste loading without significantly influencing its leachability. Large radiation doses do not affect other glass durability. Devitrification increases leach rates up to a factor of ten. This increase is due to changes in the glass composition resulting in a change from a diffusion to a corrosion mechanism for leaching of the glass. Even with devitrification long range estimates indicate that only small releases of material occur with the leaching of zinc borosilicate waste glasses. As new waste compositions are introduced, new glass formulations are developed for the solidification of the wastes.

REFERENCES

1. W. A. Ross, Development of Glass Formulations Containing High-Level Nuclear Wastes, BNWL-SA-6071, Battelle, Pacific Northwest Laboratories, Richland, WA, to be published.

2. R. P. Turcotte and J. W. Wald, Devitrification Behavior in Nuclear Waste Glass, BNWL-SA-6060A, Battelle, Pacific Northwest Laboratories, Richland, WA, to be published.

TABLE 1

COMPOSITION OF ZINC BOROSILICATE WASTE GLASS

	GLASS COMPOSITION	FRIT COMPOSITION
SiO_2	27	37
B_2O_3	11	15.1
ZnO	21	28.9
Na_2O, K_2O	8	11
CaO, MgO, SrO, BaO	6	8
FISSION PRODUCT OXIDES	23	
ACTINIDES	1	
REPROCESSING CHEMICALS	3	

FIGURE 1.

LEACH RATE VS CALCINE CONTENT

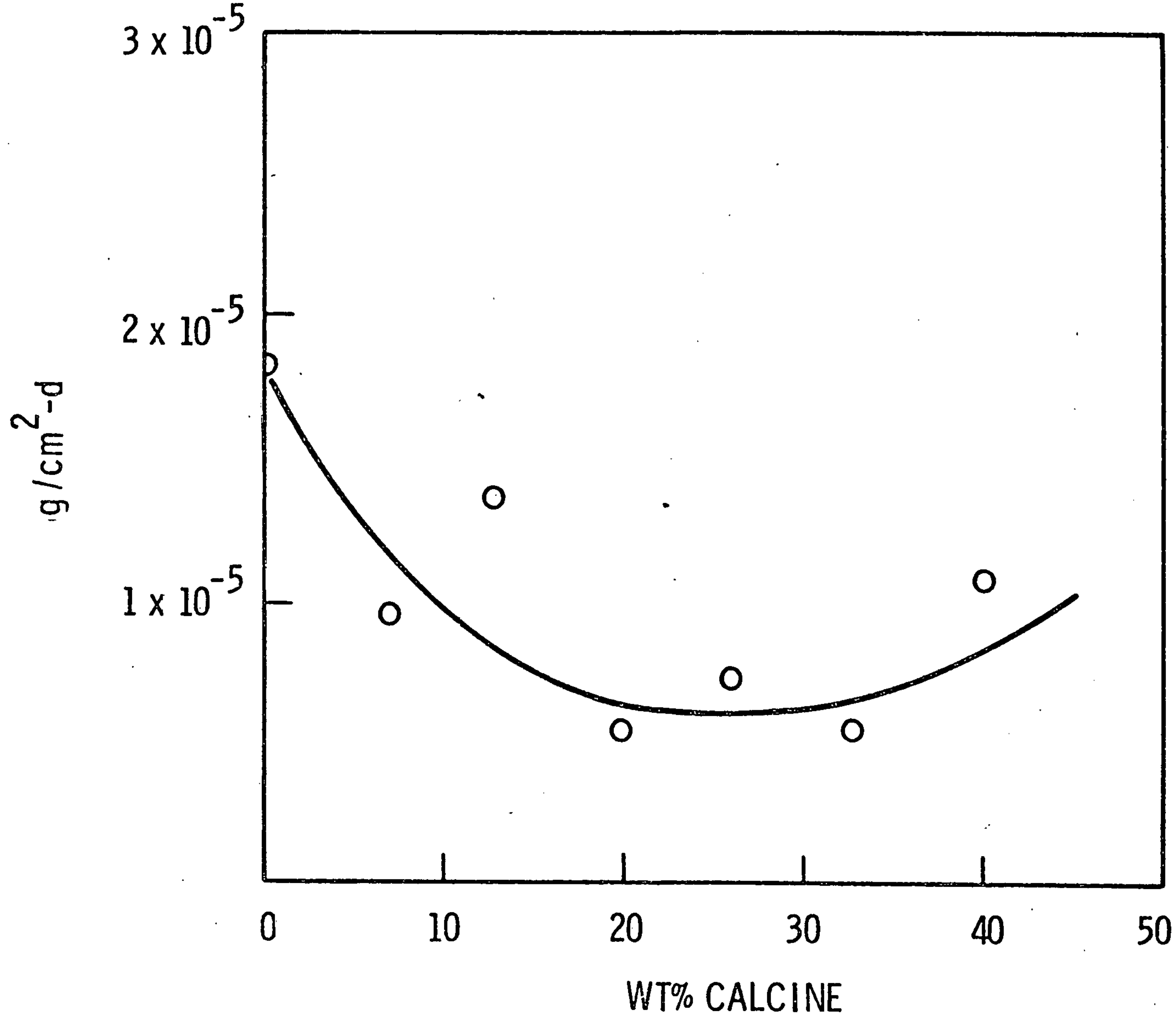


FIGURE 2.

SOXHLET EXTRACTOR LEACH TEST APPARATUS

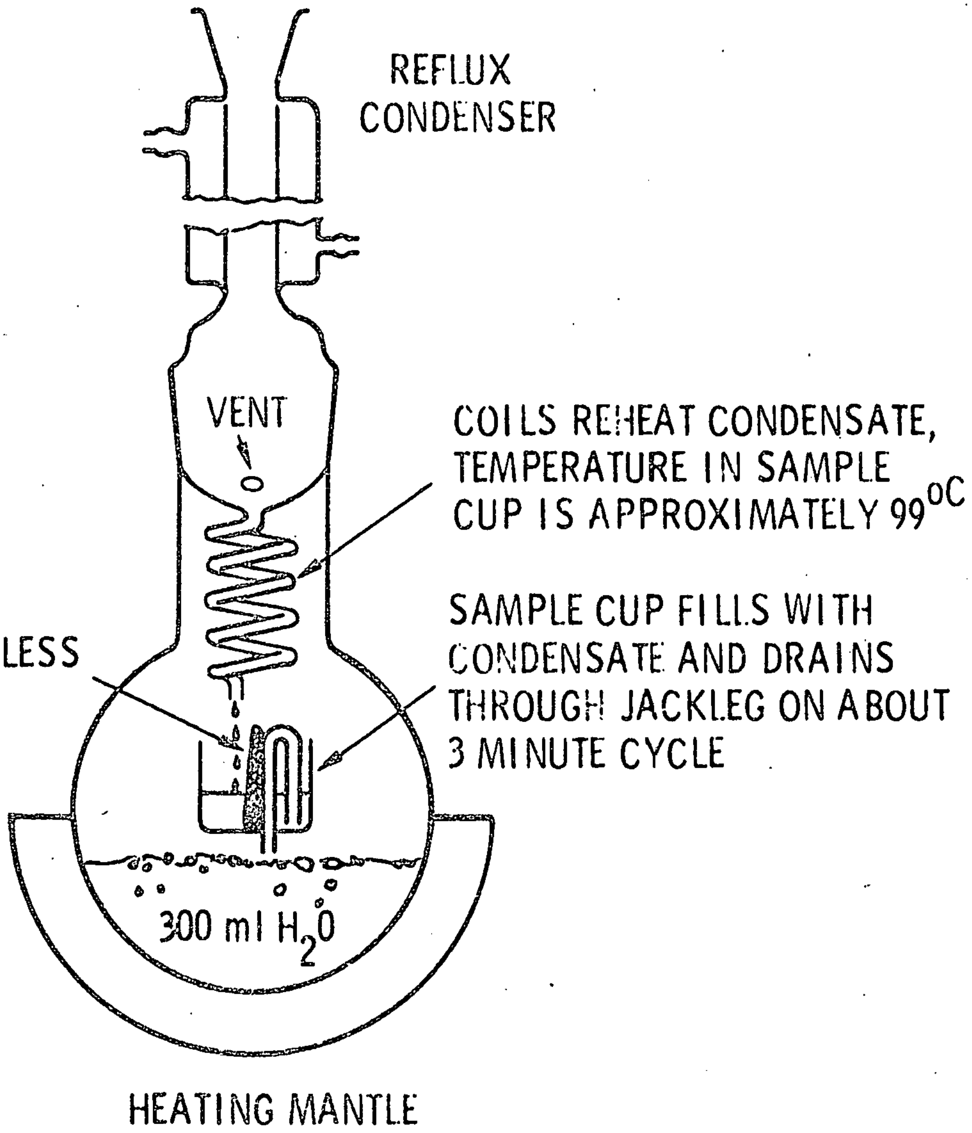


FIGURE 3.

IAEA LEACH TEST APPARATUS

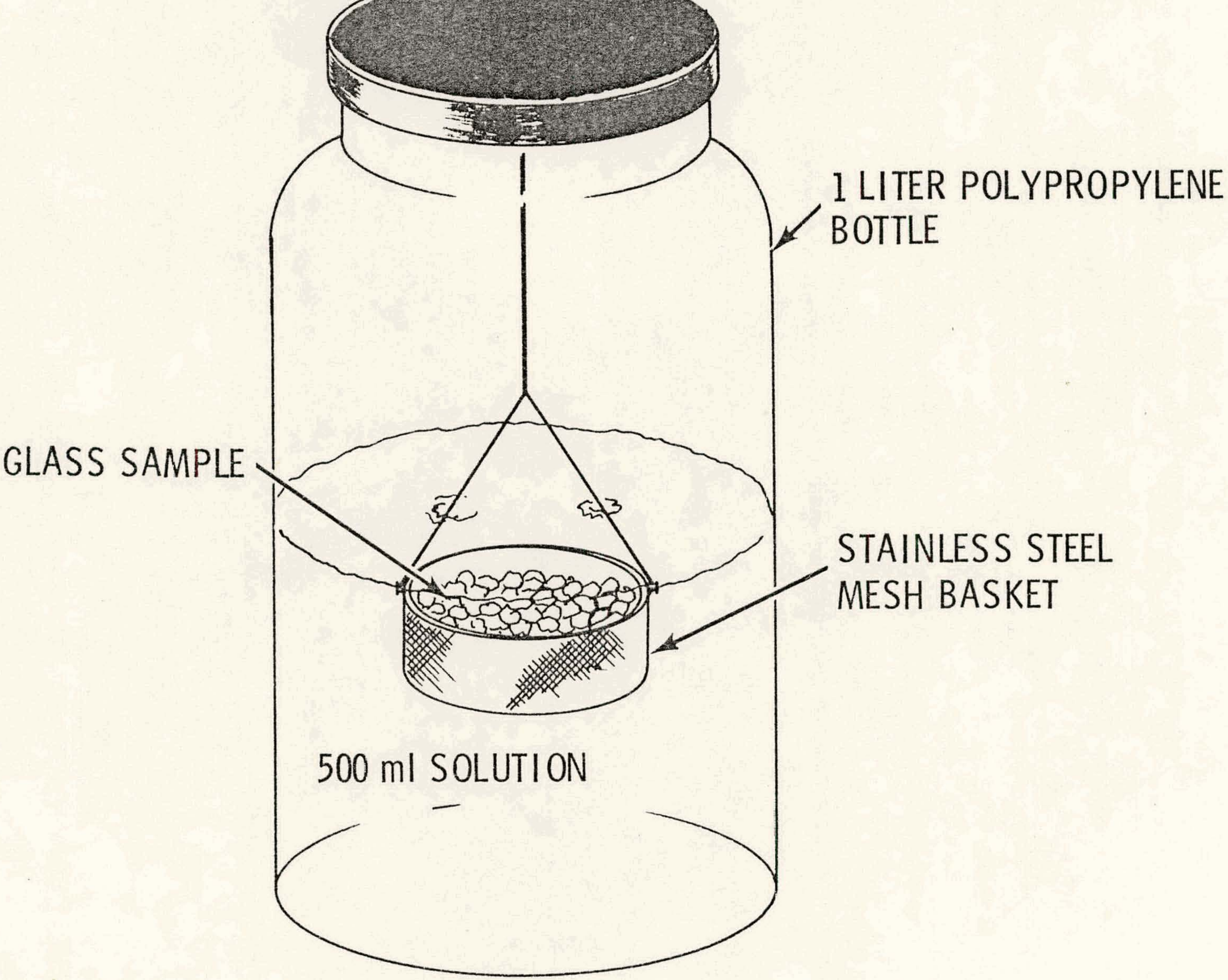


FIGURE 4.

FLOW EFFECTS

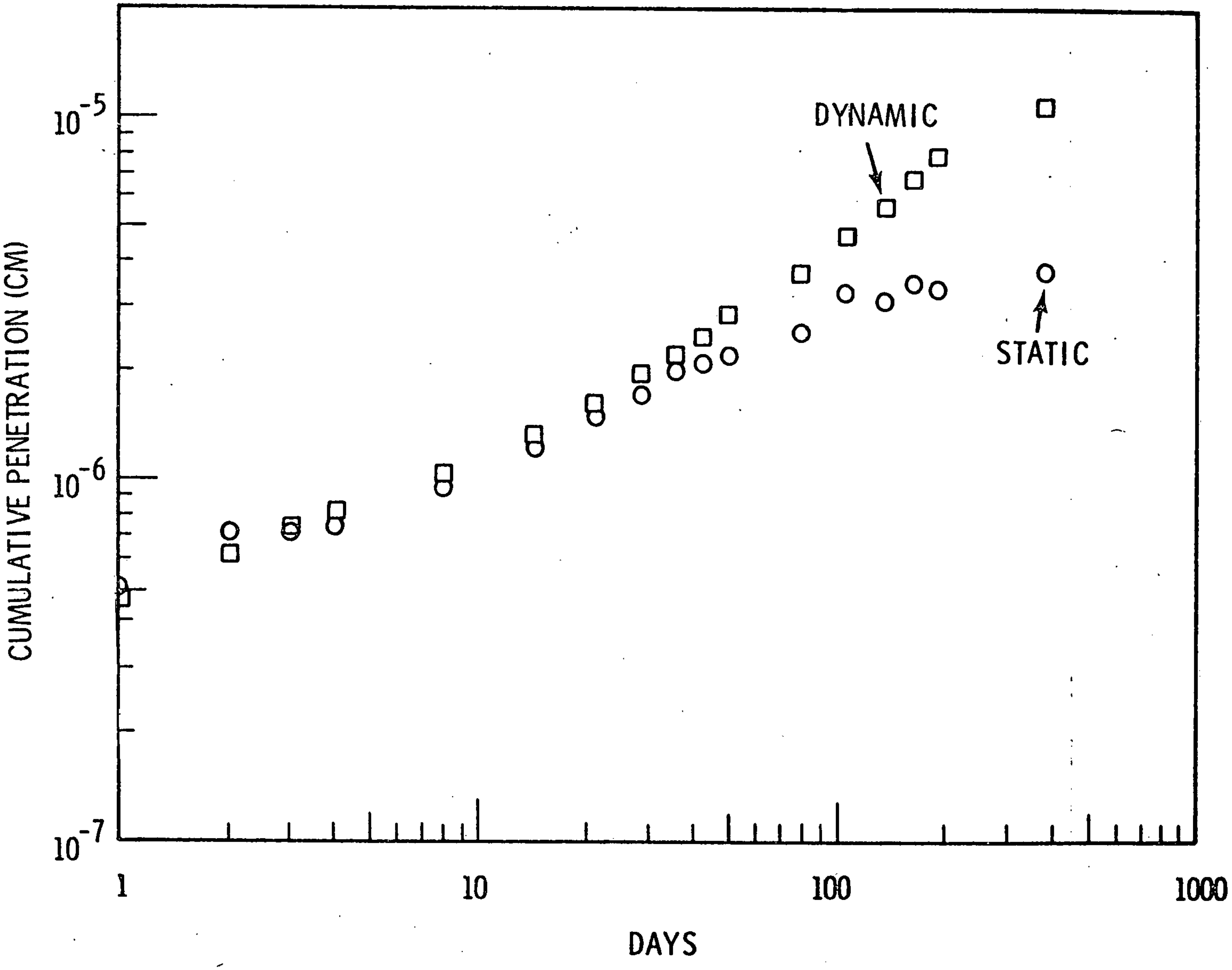


FIGURE 5.

LEACHABILITY OF ^{244}Cm-DOPED HIGH-ZINC BOROSILICATE WASTE GLASS

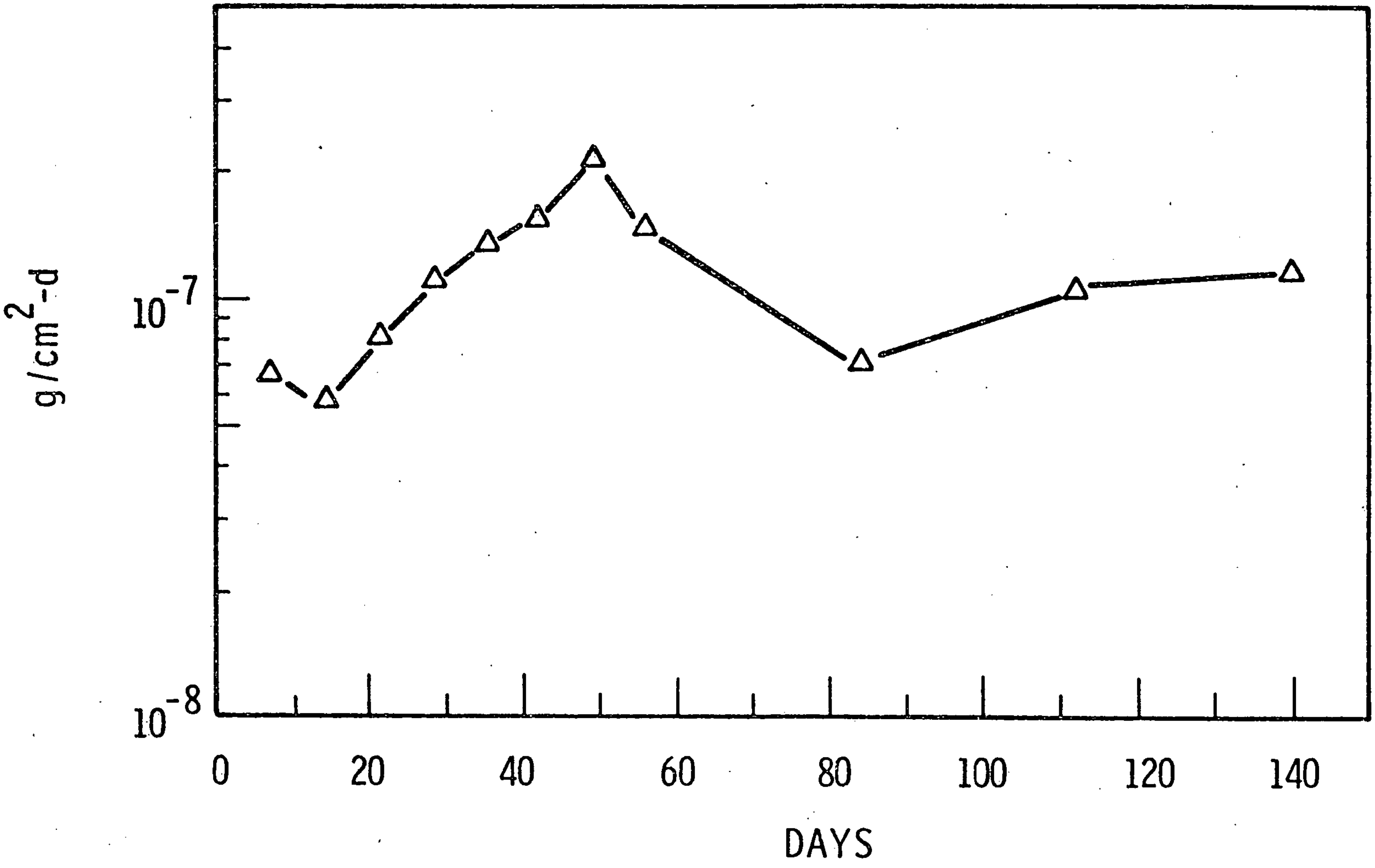


FIGURE 6.

RADIOACTIVE WASTE GLASS LEACH RATES

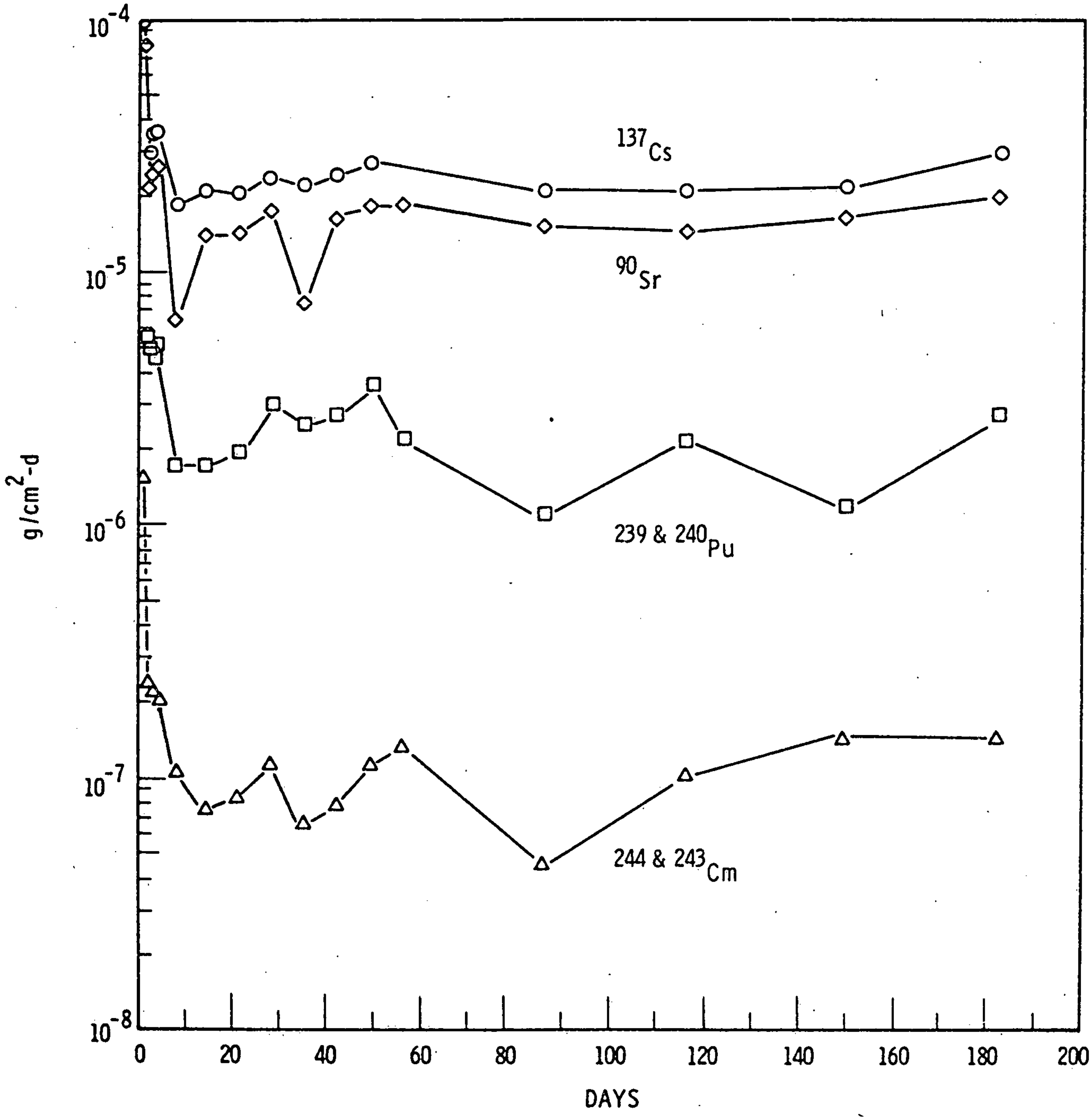


FIGURE 7.

DEVITRIFICATION EFFECTS

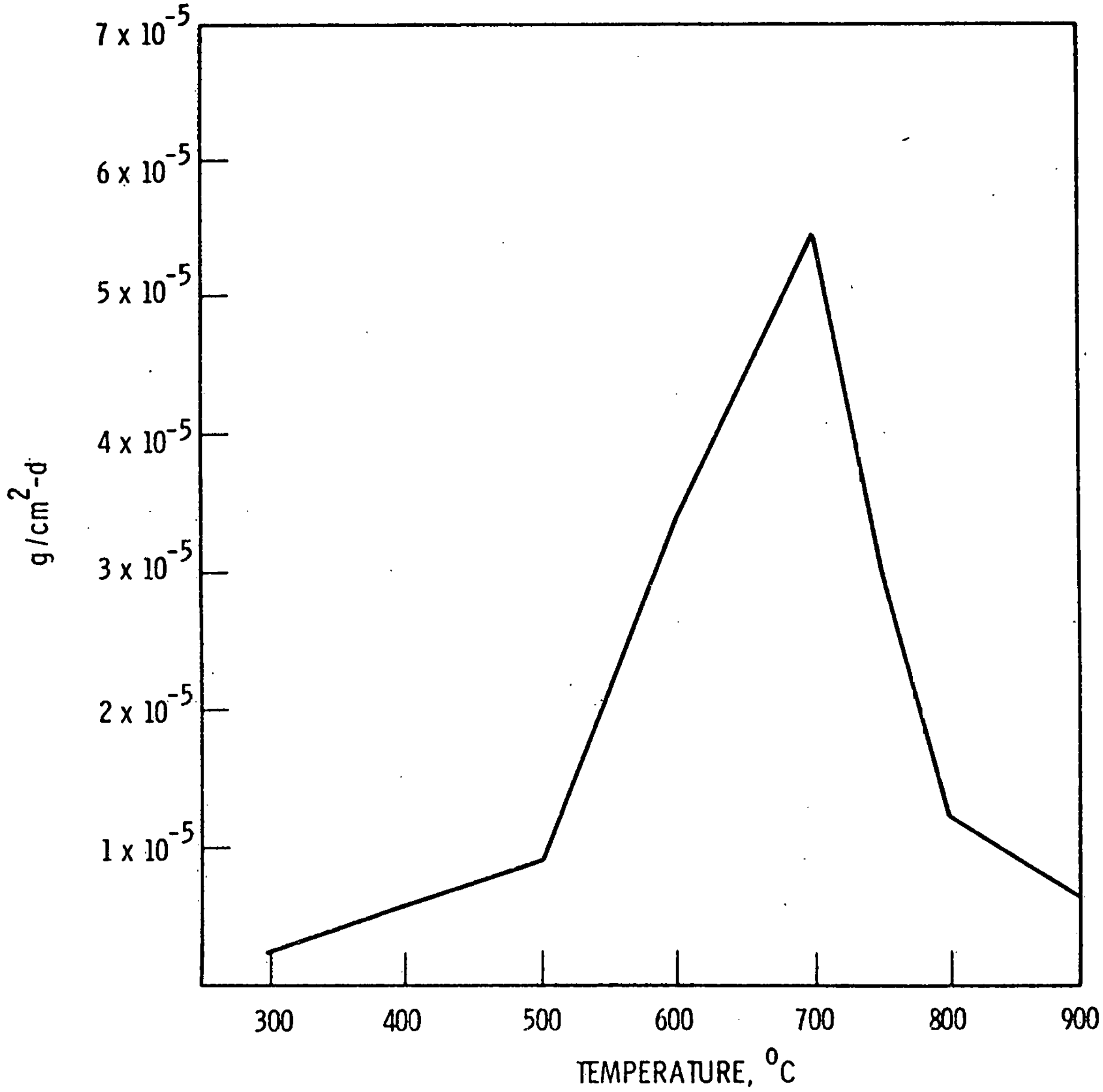
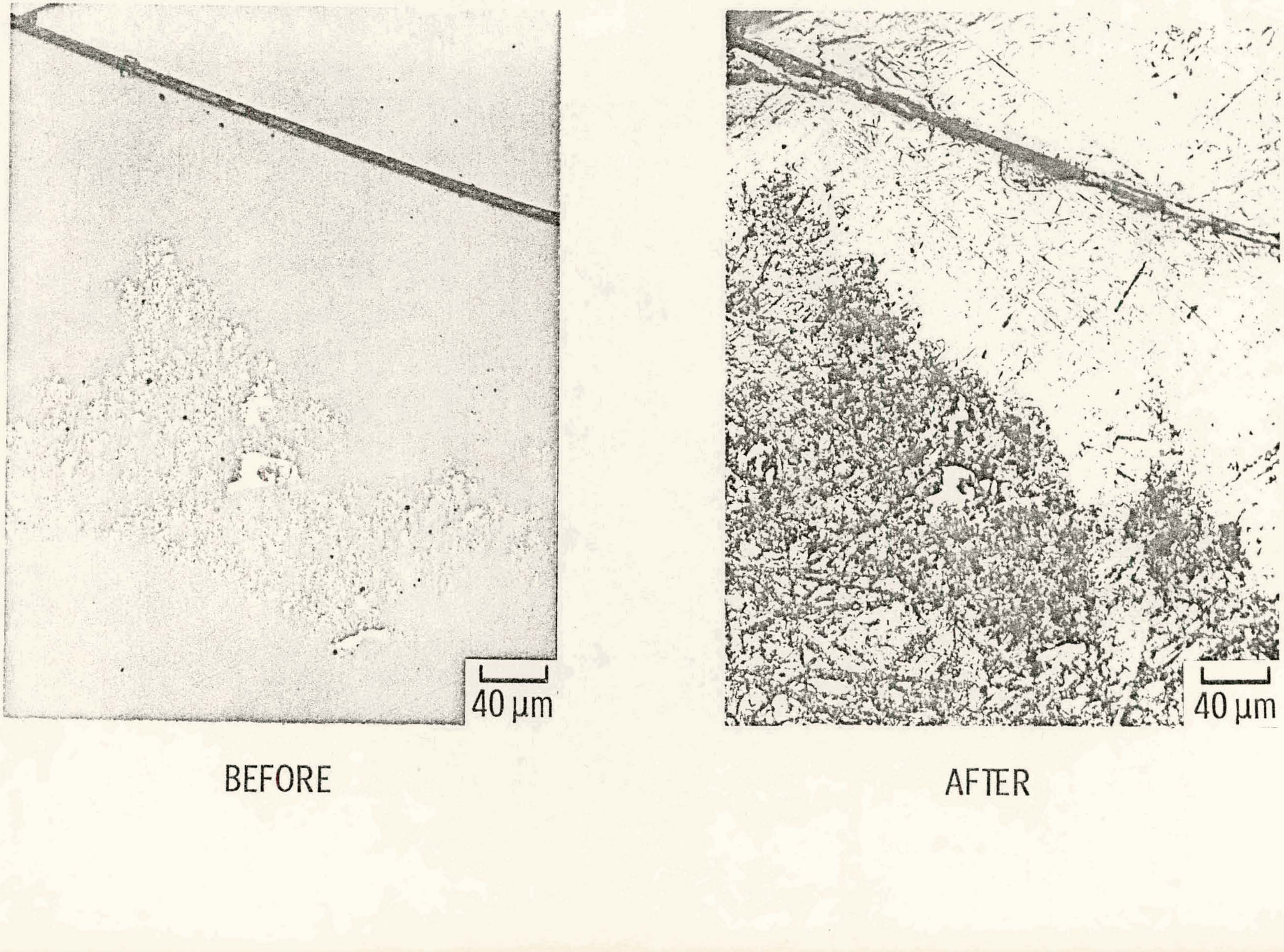


FIGURE 8.

LEACHING REACTIONS - VITREOUS WASTE GLASS

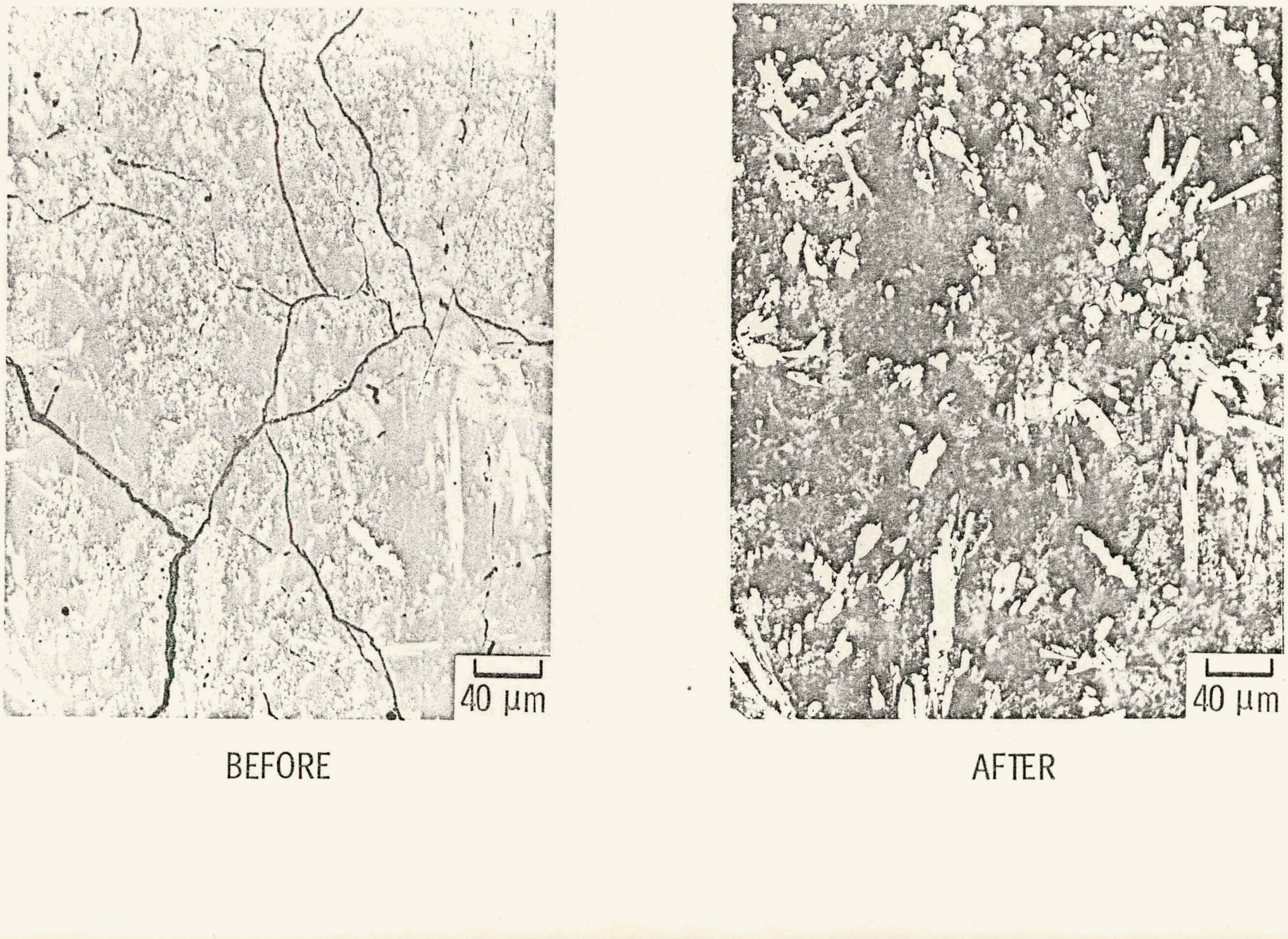


BEFORE

AFTER

FIGURE 9.

LEACHING REACTIONS - DEVITRIFIED WASTE GLASS



BEFORE

AFTER

FIGURE 10.

LONG TERM LEACH RATE

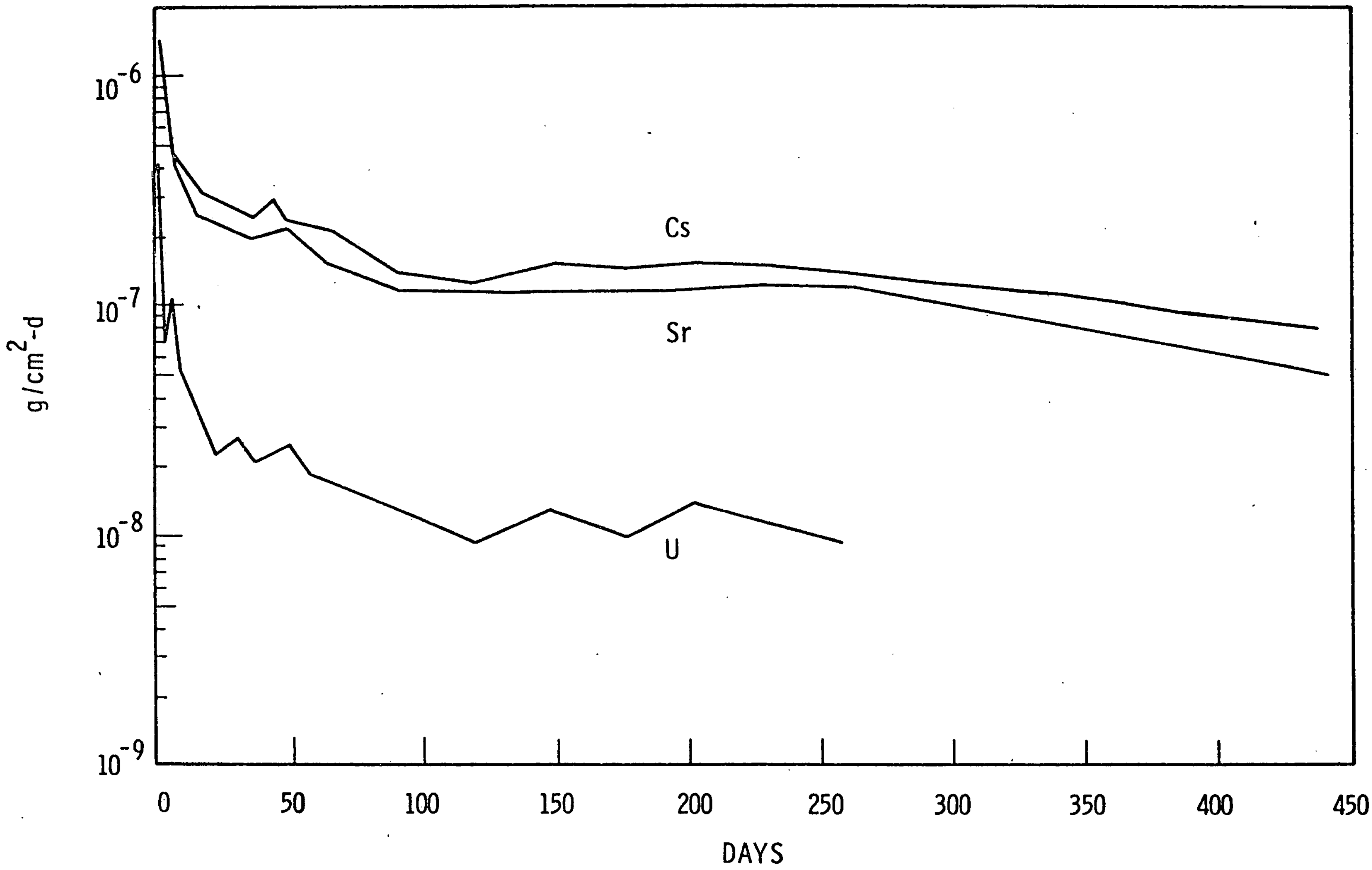


FIGURE 11.

CUMULATIVE PENETRATION VS TIME BASED ON CESIUM BEHAVIOR