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LONG TERM LEACHING OF IRRADIATED
SPENT FUEL

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ABSTRACT

Spent Light Water Reactor (LWR) fuel with burnups of 9, 28 and 54 MWd/kg U were leach tested at 25°C in deionized water in a Paige apparatus. No discernible differences in leach rates were observed due to burnup. Additionally, the 28 MWd/kg U fuel was IAEA leach tested in five different leachants using the IAEA method. Deionized water gave the highest leach rates and a calcium chloride solution gave the lowest leach rates. An accelerated leaching period was observed during the Paige leach test of the 54 MWd/kg U spent fuel.

Comparison between spent fuel and borosilicate waste glass leach rates were made. In sodium bicarbonate solution the leach rates are near equal and the glass becomes increasingly more durable with CaCl_2 solution, followed by sodium chloride solution, WIPP B brine and deionized water where the glass is two to three orders of magnitude more leach resistant than spent fuel.

LONG TERM LEACHING OF IRRADIATED SPENT FUEL

INTRODUCTION

In 1975, the Pacific Northwest Laboratory (PNL), operated by Battelle Memorial Institute, started a spent Light Water Reactor (LWR) fuel leaching study for the Department of Energy (DOE). This study was designed to yield radionuclide release rates on spent LWR fuel caused by the action of water. The results allowed comparison of leach resistance with solidified nuclear waste forms being designed and engineered at PNL, and also allowed the estimation of radionuclide releases from accident scenarios where the fuel core contacts water.

There are many types of leach tests being used to evaluate solidified waste forms (Mendel 1973). At PNL the Paige procedure (Paige 1966) was chosen for leaching radioactive samples of solidified product from the Waste Solidification Engineering Prototype (WSEP) Program (McElroy, et al. 1972). The first leach tests of spent LWR fuels were in these Paige leach systems. In 1977, spent fuel leach tests were started using a modification of the International Atomic Energy Association (IAEA) procedure. In 1979, spent fuel leach tests were started using a static leach test procedure.

The IAEA and static leach tests are part of the Waste Isolation Safety Assessment Program, a project sponsored by the Office of Nuclear Waste Isolation. The purpose of this program is to gather experimental data and develop models to assess the safety of nuclear waste isolation in geologic formations.

In this paper we will present spent fuel leach data from the Paige tests and IAEA tests. The contents are extracted from two more detailed publications (Katayama, 1979; Katayama, et al., 1979).

EXPERIMENTAL PARAMETERS

Two leaching procedures (Paige and IAEA) were used to generate the data presented in this paper. The Paige test apparatus is shown in Figure 1. In this system the leachant is recirculated with an airlift pump at a flow rate of 75 liters/day. The leachant is changed at the time of sampling. Sampling was done daily for the first week, weekly for three weeks, and monthly thereafter. Plateout samples for the Paige apparatus have not been taken. However, analytical samples are acidified to prevent plateout in the sample bottles.

The IAEA leach apparatus is shown in Figure 2. In this system the leachant is static during the leaching interval between sampling periods. The IAEA sampling period is daily for the first week, weekly for 8 weeks, monthly for 6 months, and then semi-annually. Plateout samples were taken and analytical samples were acidified to prevent plateout in the bottles.

All the leach tests to date have been with unclad fuel in the form of fuel fragments (Figure 3). The fuels used in the Paige leach tests were from three different reactors and had different average burnups. The Zorita Reactor fuel had a burnup of 54.5 MWd/kg U, the H. B. Robinson-II Reactor fuel had a burnup of 28.0 MWd/kg U, and the Quad Cities-I Reactor fuel had a burnup of 9.0 MWd/kg U. Only one fuel burnup (H.B. Robinson-II Reactor fuel with a burnup of 28.0 MWd/kg U) was leached in the IAEA apparatus. The IAEA tests were in the following five leach solutions: 1) deionized water, 2) 1.76 g/l NaCl, 3) 1.66 g/l CaCl, 4) 2.52 g/l NaHCO₃, and 5) saturated WIPP B salt brine.

The leach rates presented in this paper are all periodic leach rates and are calculated from the following equation:

$$\text{leach rate} = \frac{a_n}{A_0} \cdot \frac{w}{s} \cdot \frac{1}{t_n} = \text{grams of solids/cm}^2\text{-d} \quad (1)$$

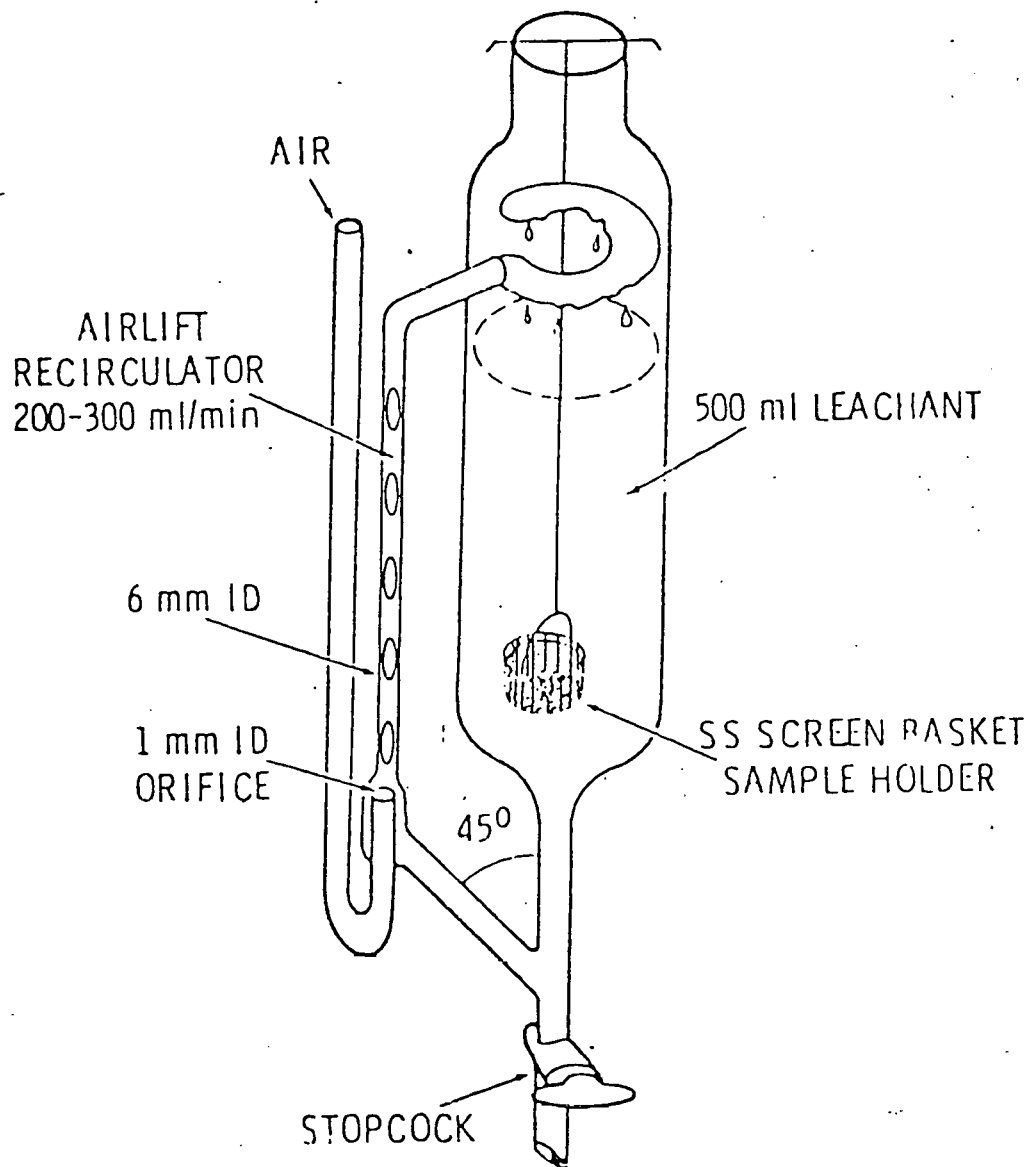


FIGURE 1. Paige Leach Test Apparatus Used at the Pacific Northwest Laboratory

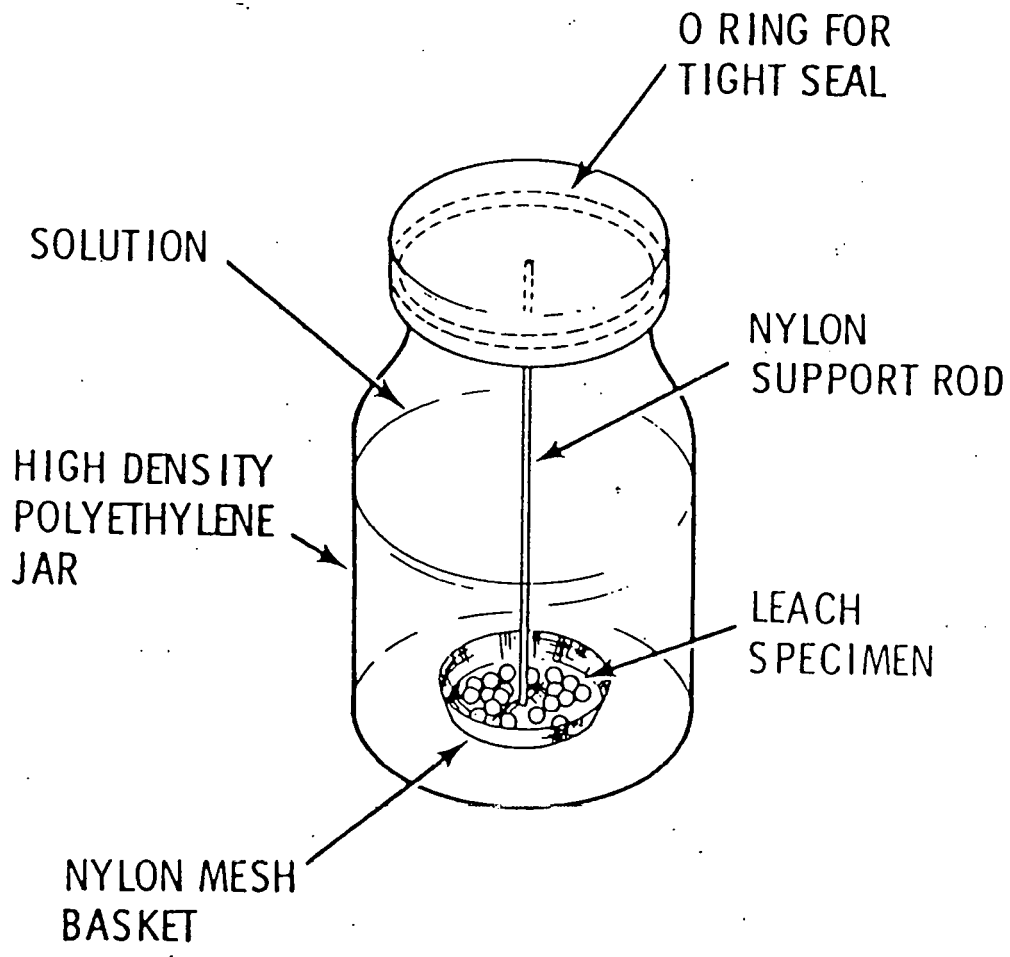


FIGURE 2. IAEA Leach Test Container

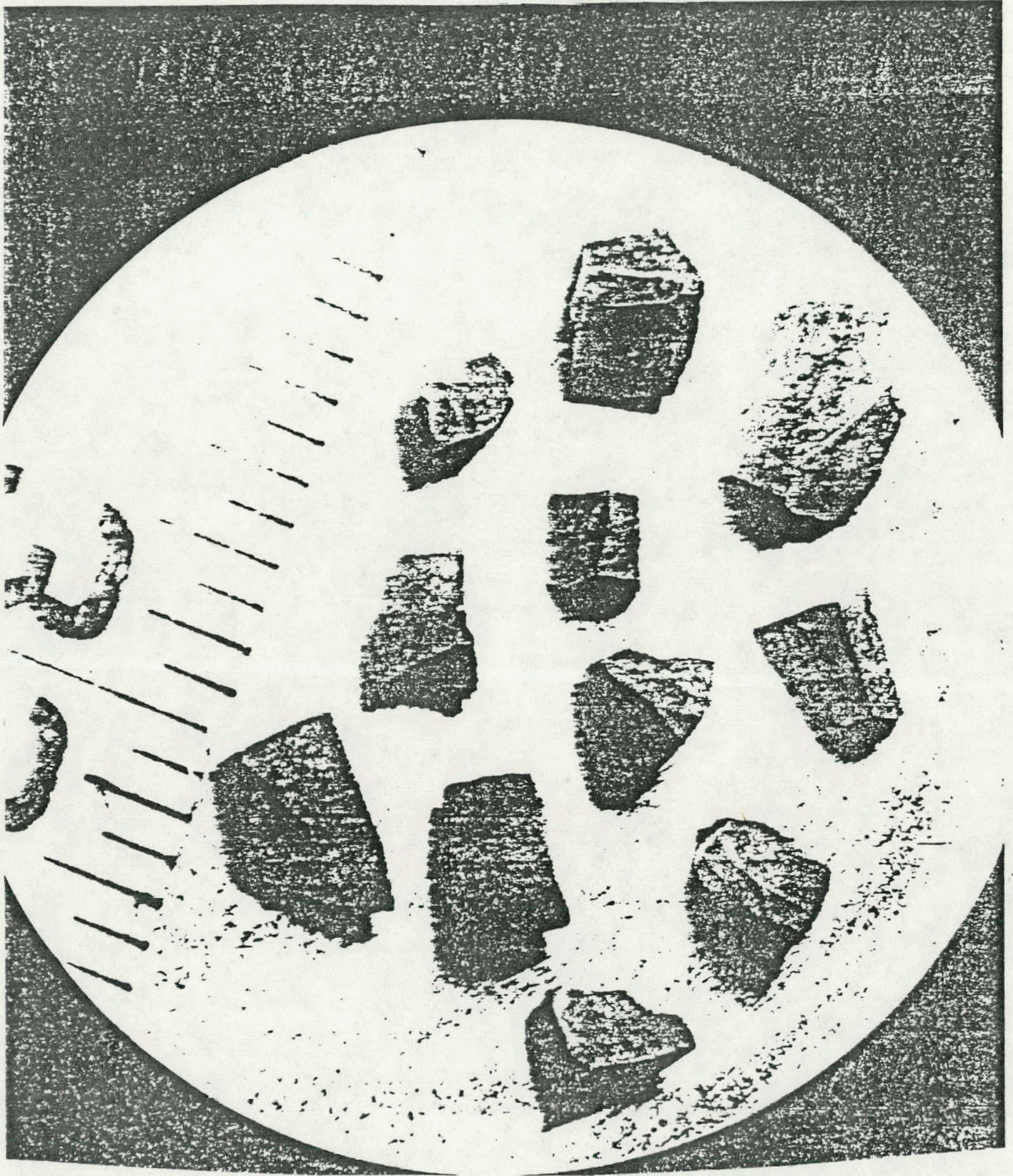


Figure 3. Spent LWR Fuel Fragments Photographed Through Hot-Cell Periscope (each division on scale equals 1/16 inch)

where: a_n = amount of specific radioisotope leached in time t_n
 A_0 = amount of specific radioisotope initially present in fuel sample
 w = weight of sample, g
 s = geometric surface area of sample, cm^2
 t_n = duration of n^{th} leach period, days.

The cumulative fraction of radionuclide released to the leachant is calculated by the following equation:

$$\text{fraction released} = \frac{\sum a_n}{A_0} \quad (2)$$

where: a_n = amount of specific radioisotope leached in time n
 A_0 = amount of specific radioisotope initially present in fuel sample

The experimental uncertainties associated with leach tests on fuel fragments in a shielded facility and the radiochemical analysis of the leachant are of many origins (Mendel, 1973). We estimate the experimental uncertainties for the Paige test leach rates to be about 1/2 order in magnitude for the cesium, and about one order in magnitude for the plutonium, uranium and curium.

RESULTS AND DISCUSSION

Paige test leach rate data for the 54.5 MWd/kg U fuel in deionized water at 25°C are shown in Figure 4 for duplicate samples Z-6 and Z-7. The curves for the period up to approximately 550 days appear as continuations of the data reported after 140 days (Katayama, 1976) and are selective with respect to the radionuclides. From 600 days to 800 days the curves converge and the leach rates for all the radionuclides become nearly equal. This period is characterized by a hump in the leach rate curves and is referred to as the "accelerated leaching period" in this paper. After 750 days the leach rates start to decrease in value.

Not shown in Figure 4 are the leach rate curves for ^{144}Ce and ^{154}Eu , which were not continuous leach curves. These radionuclides were analytically detected during the first 200 days of the leach test and then were not radiochemically detectable until the start of the accelerated leaching period. The reappearance of ^{144}Ce and ^{154}Eu during the congruent leaching period indicate that new sources of these radionuclides are available--probably new fuel surfaces are exposed. Additional experimental work is being done at PNL to better understand the release mechanism of radionuclides from spent fuel.

Graphical representation of fractional release of ^{137}Cs , $^{239+240}\text{Pu}$, and ^{244}Cm , as a function of days leached, are shown in Figures 5, 6 and 7, respectively. After 1013 days of leaching, 1.72% of the cesium, 0.35% of the plutonium, and 0.28% of the curium were released to the deionized water. The change from selective leaching to accelerated leaching is most pronounced for the ^{244}Cm release curve (Figure 7), where the fraction released increased by 3 orders of magnitude.

Spent LWR fuel with a burnup of 54.5 MWd/kg U is being leach tested in a synthetic sea brine. Cesium-based leach rate data for 652 days of cumulative leaching in brine and deionized water are shown in Figure 8. Based on the release of ^{137}Cs , the leach rate of spent LWR fuel is 1/2 order in magnitude lower in sea brine than in deionized water.

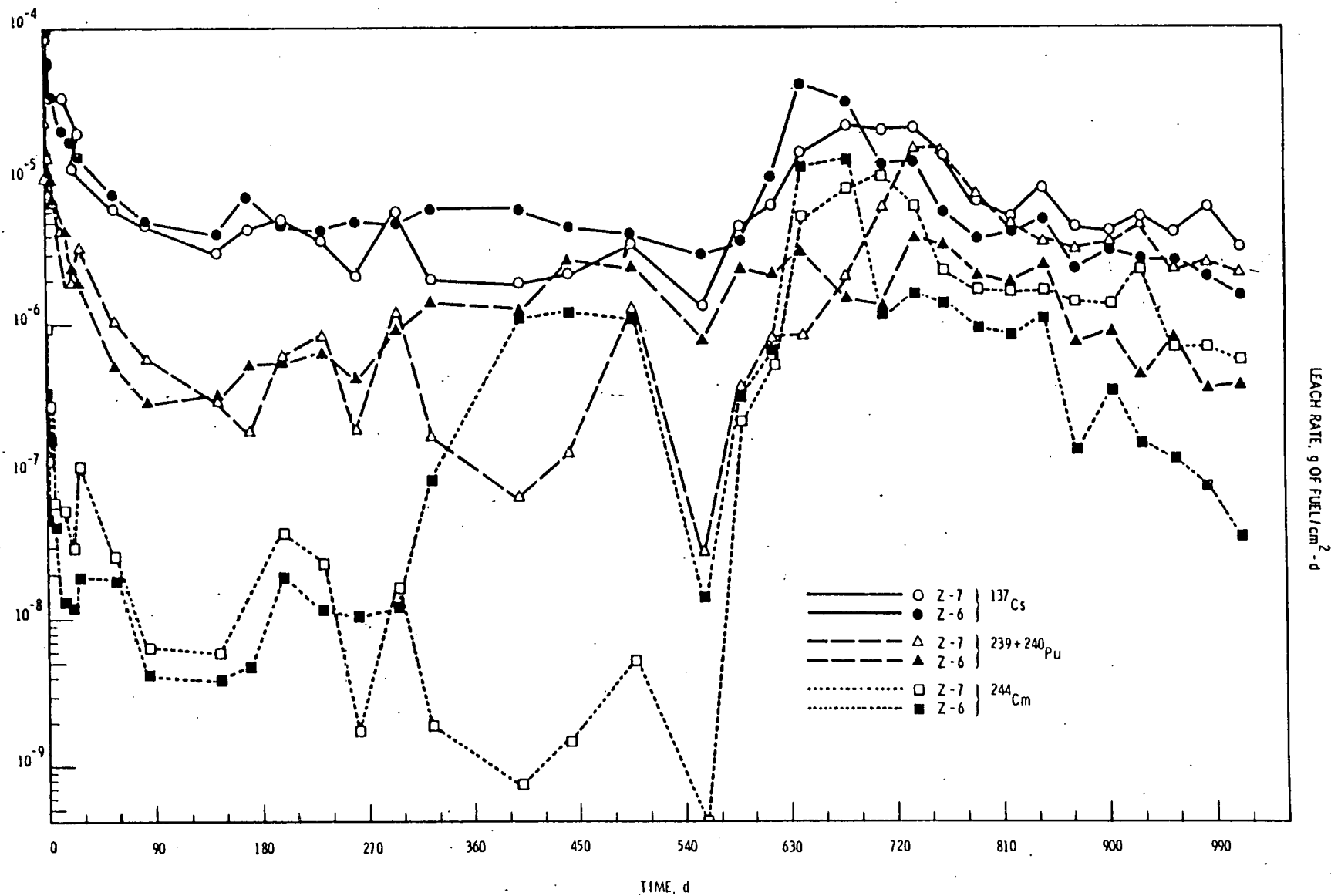


FIGURE 4. Leach Rate of 54.5 MWd/kgU Spent LWR Fuel in Deionized Water at 25°C. Duplicate samples are designated Z-6 and Z-7

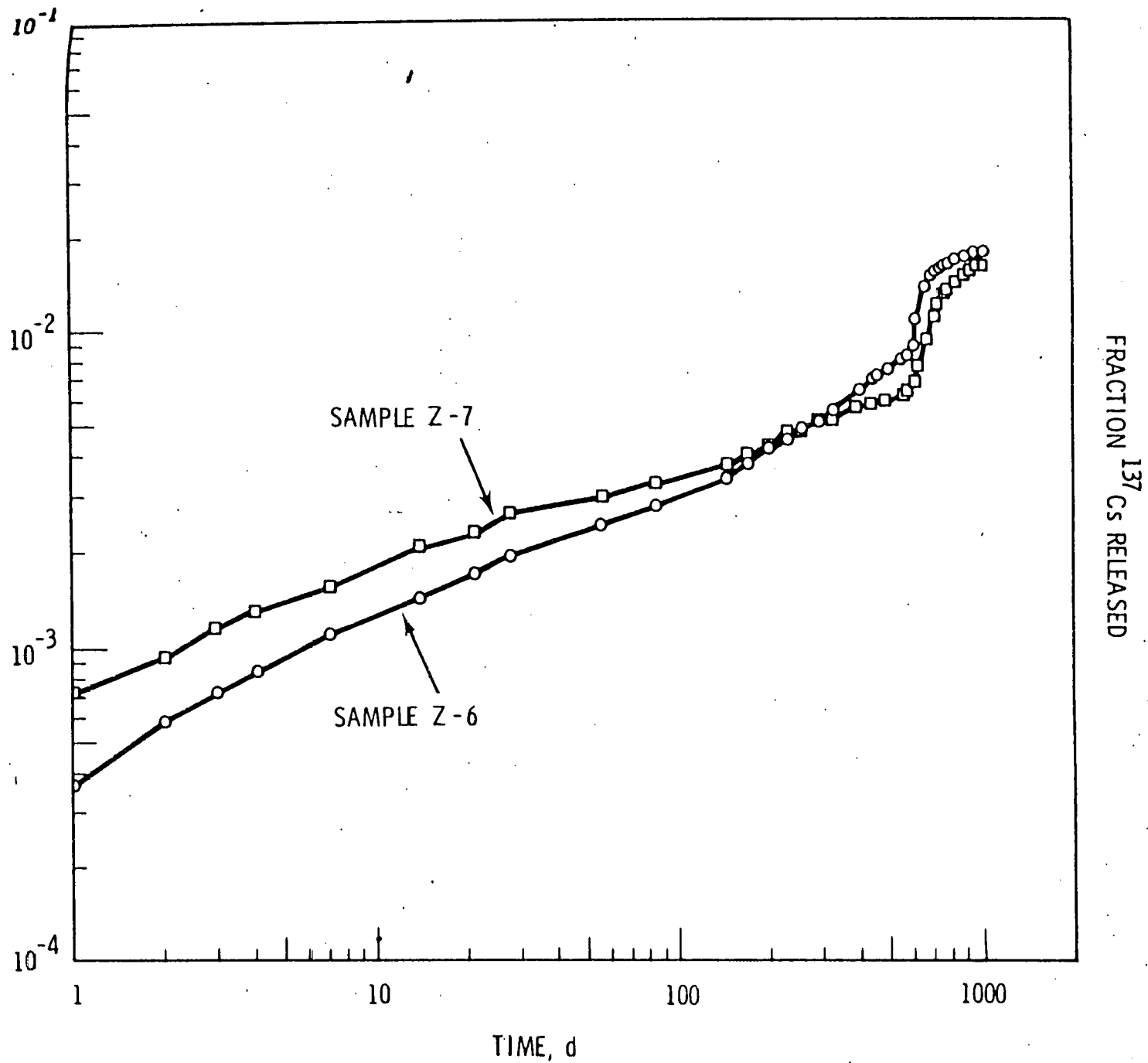


FIGURE 5. Fraction of ^{137}Cs Released from Spent LWR Fuel, 54.5 MWd/kgU, in Deionized Water at 25°C

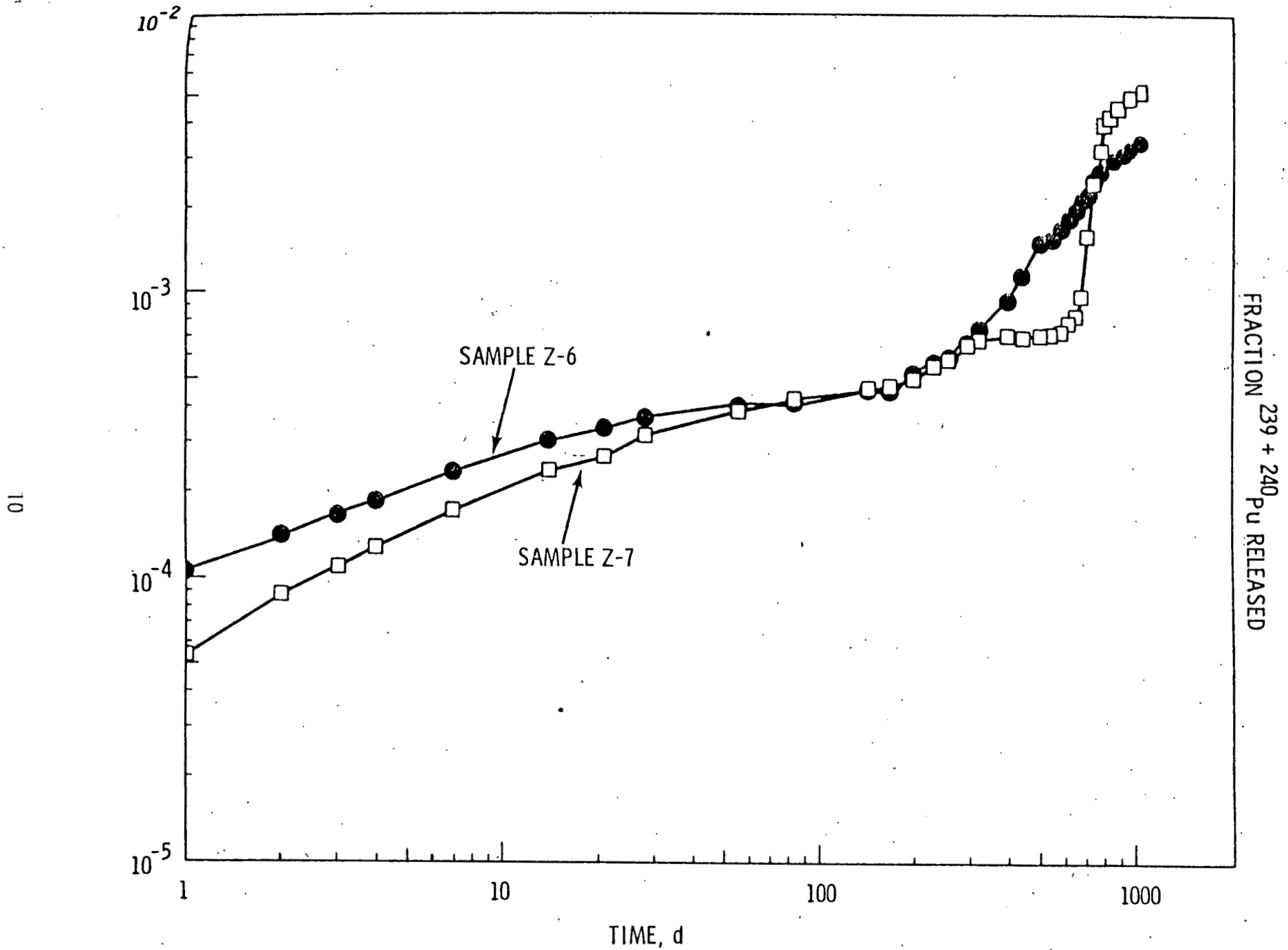


FIGURE 6. Fraction of $^{239}+^{240}\text{Pu}$ Released from Spent LWR Fuel, 54.5 MWd/kgU in Deionized Water at 25°C

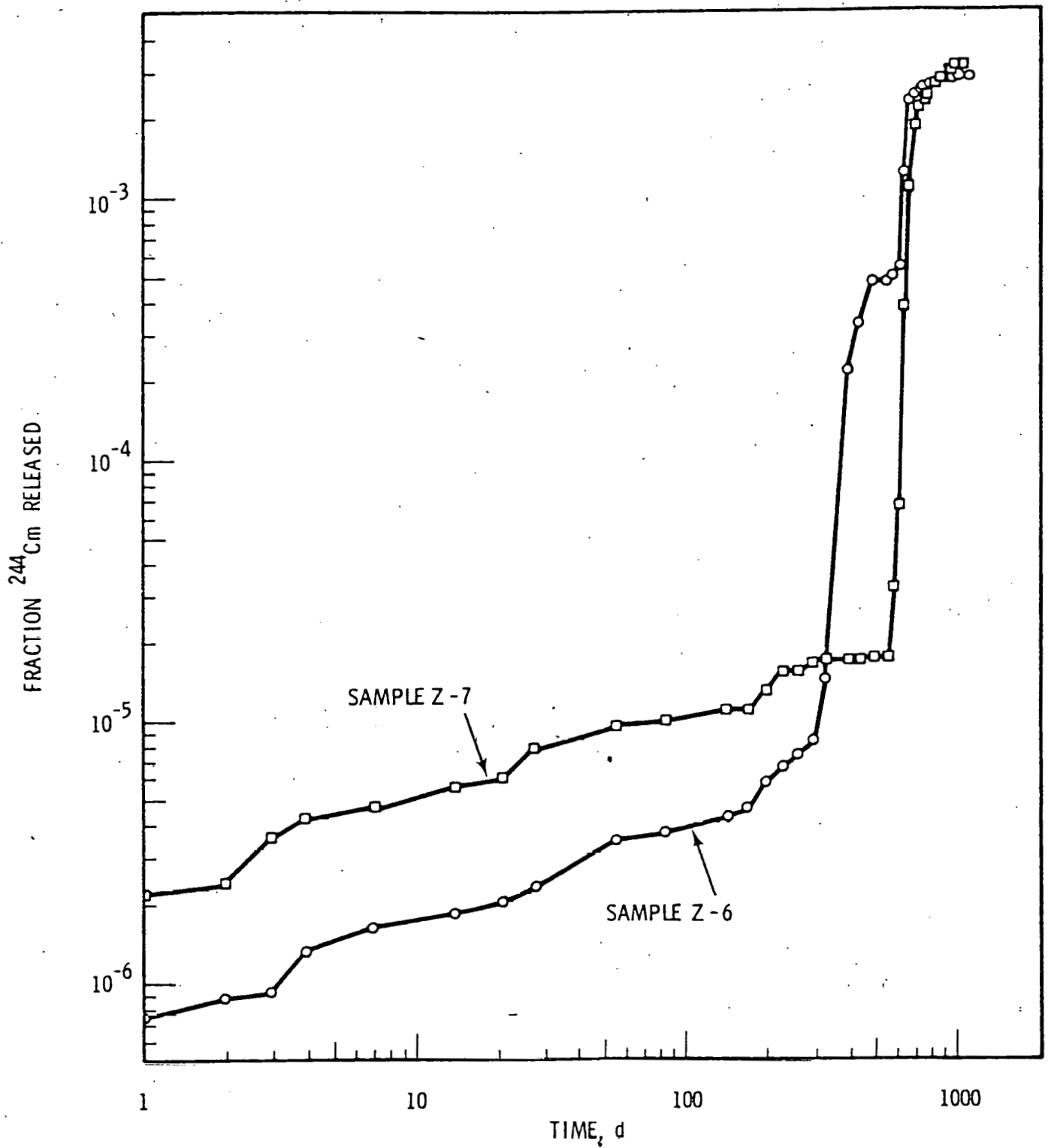


FIGURE 7. Fraction of ^{244}Cm Released from Spent LWR Fuel, 54.5 MWd/kgU, in Deionized Water at 25°C

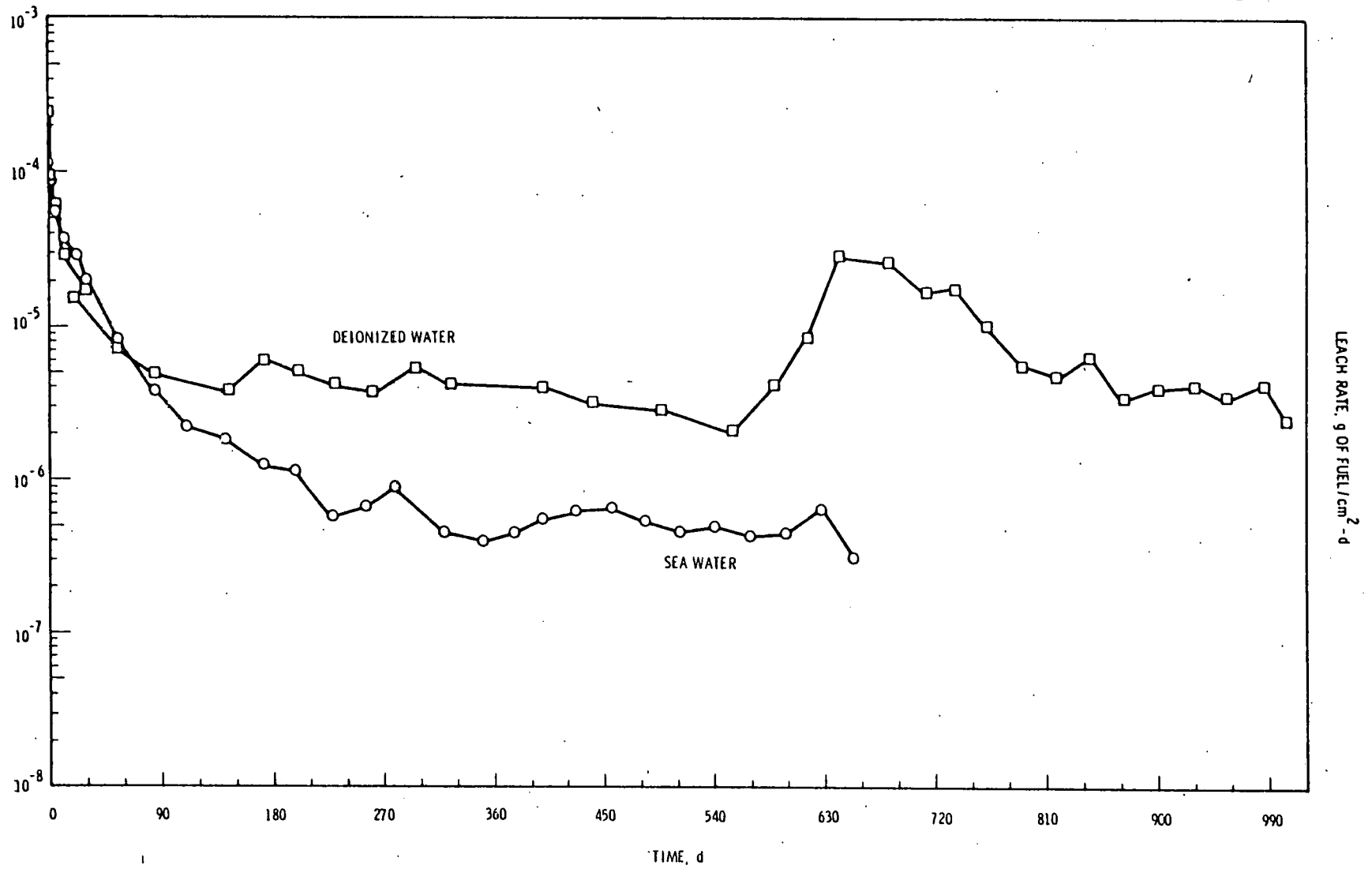


FIGURE 8. Leach Rate of 54.5 MWd/kgU Spent LWR Fuel Based on Release of ¹³⁷Cs in Sea Brine and Deionized Water at 25°C

Spent LWR fuels with three different burnups (54.5, 28.0 and 9.0 MWd/kg U) are being leached in deionized water at 25°C. Figures 9, 10, 11 and 12 show leach rate curves for these fuels based on the release of ^{137}Cs , $^{239+240}\text{Pu}$, total uranium, and ^{244}Cm , respectively. The spread in the curves shown in Figures 9, 10 and 11 are about equal to the experimental uncertainties for the radionuclides shown. Burnup appears to have no effect upon the leach rate based on release of ^{137}Cs , $^{239+240}\text{Pu}$ and total uranium. The curium-based leach rates are spread out beyond the estimated experimental uncertainties. Further work is needed to understand the release of curium from spent fuel.

The IAEA leach rate data for the 28.0 MWd/kg U fuel in 5 different leachants at 25°C are shown in Figures 13, 14 and 15 for ^{137}Cs , $^{239+240}\text{Pu}$, and ^{244}Cm . The highest leach rates are in deionized water and the lowest in CaCl_2 solution.

Comparison of IAEA and Paige leach rates at a cumulative time of 467 days shows about one order difference (higher in IAEA compared to Paige) in the values for releases based on ^{137}Cs , $^{239+240}\text{Pu}$, and ^{244}Cm . The difference may be due to radionuclide plateout on the Paige apparatus which was not measured.

Paige leach rates for spent fuel (deionized water at 25°C) were found to be comparable to the first generation borosilicate glasses vitrified during the WSEP demonstration at PNL (Katayama 1976). Comparison spent fuel and glass leach rates using the IAEA procedure are tabulated in Table I. The ^{244}Cm and ^{239}Pu based glass leach rates are for a 76-68 borosilicate glass (Bradley, Harvey and Turcotte 1979). In the reference deionized water leachant the spent fuel leach rate is two to three orders of magnitude higher than glass. These differences decrease as you go from deionized water to WIPP B brine to NaHCO_3 solution to NaCl solution and become nearly equal in NaHCO_3 solution.

TABLE I. Comparison of IAEA Leach Rates (g/cm²-d) at 25°C

	²³⁹ Pu (1)		²⁴⁴ Cm (2)	
	76-68 Glass	Spent Fuel	76-68 Glass	Spent Fuel
Deionized Water	5 x 10 ⁻⁸	2 x 10 ⁻⁵	4 x 10 ⁻⁷	2 x 10 ⁻⁵
WIPP B Brine	2 x 10 ⁻⁸	2 x 10 ⁻⁶	1 x 10 ⁻⁸	3 x 10 ⁻⁶
NaCl	7 x 10 ⁻⁸	3 x 10 ⁻⁶	2 x 10 ⁻⁷	4 x 10 ⁻⁶
CaCl ₂	2 x 10 ⁻⁸	3 x 10 ⁻⁶	1 x 10 ⁻⁷	9 x 10 ⁻⁸
NaHCO ₃	2 x 10 ⁻⁷	1 x 10 ⁻⁷	2 x 10 ⁻⁷	2 x 10 ⁻⁷

(1) 151 days

(2) 454 days

The pH of the IAEA leach solutions decreased during the test for all solutions except the sodium bicarbonate solution. Figure 15 shows the uranium concentration and pH of the leachate for the sampling periods. The triangular symbols are the sodium bicarbonate results. Three UO₃(H₂O)_x solubility lines (Holland and Bush 1978) and one line representing the effect of CO₃²⁻ on uraninite dissolution (Grandstaff 1976) are also shown in the figure. Our leach solutions have not reached the solubility limit of uranium and there is no apparent chloride effect on our uranium release values. There appears to be a correlation of our uranium release data in sodium bicarbonate solution to the curve shown by Grandstaff (1976).

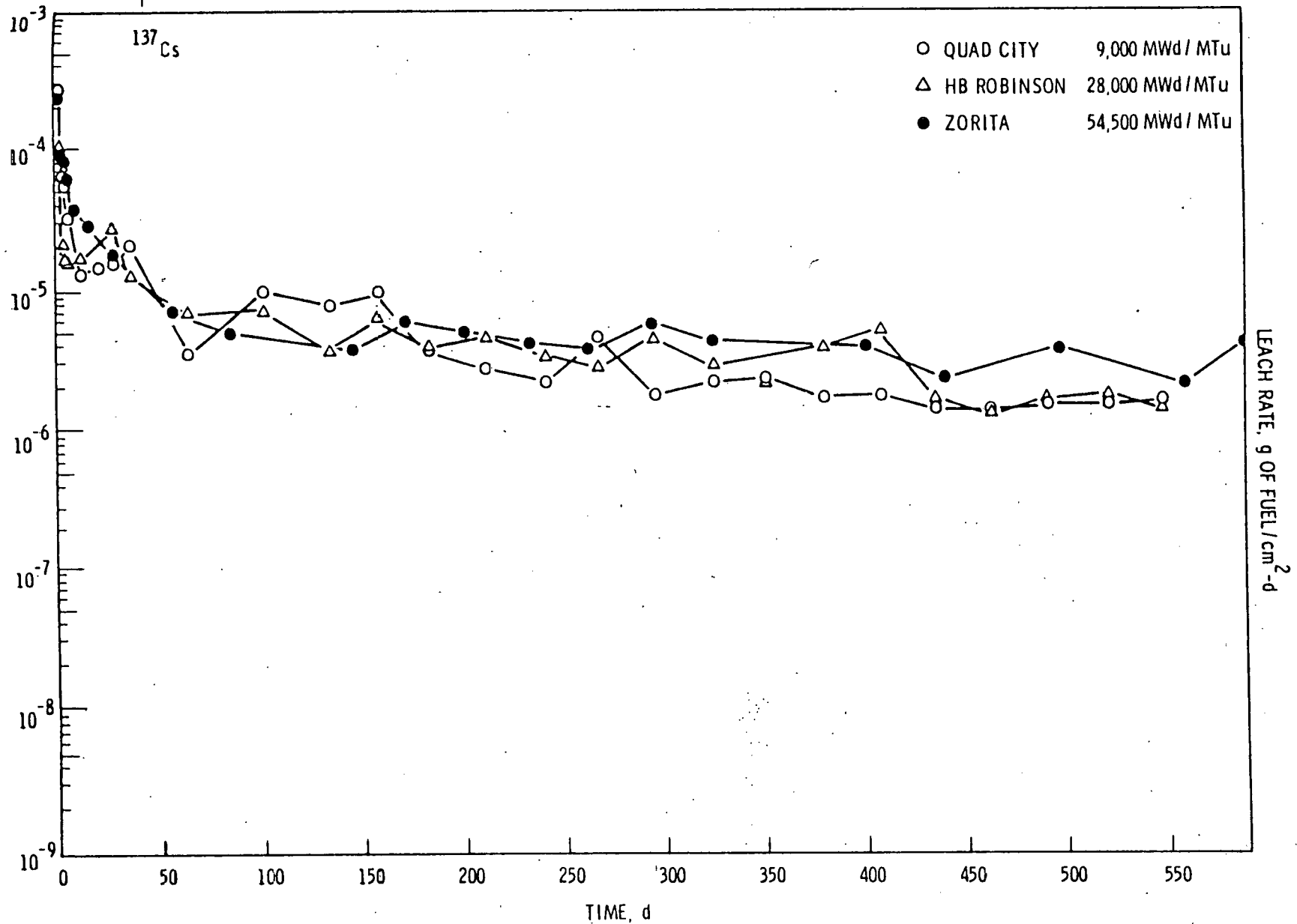


FIGURE 9. Leach Rate of Spent Fuels Based on Release of ^{137}Cs in Deionized Water at 25°C with Burnups of 9.0, 28.0 and 54.5 MWd/kgU

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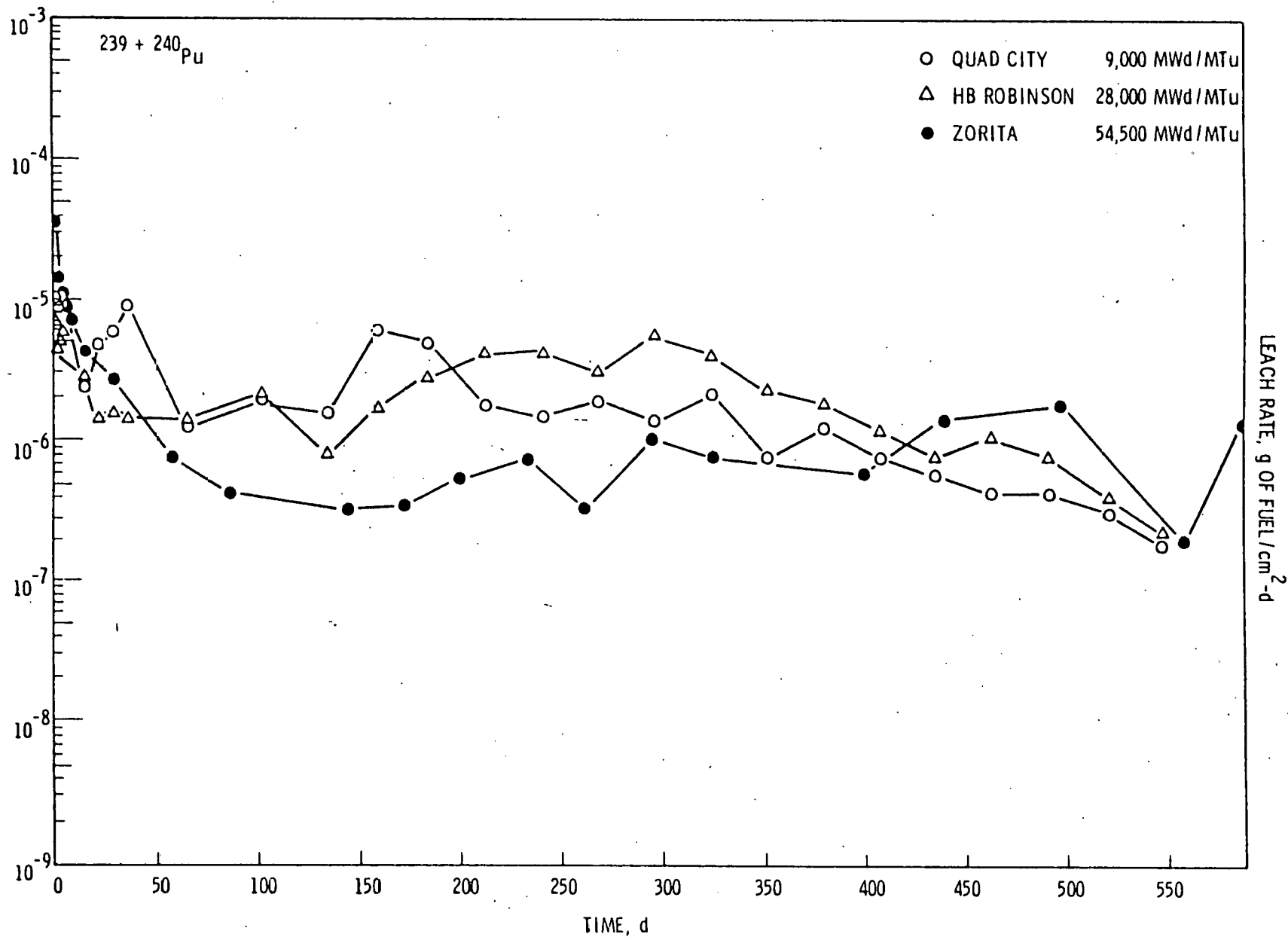


FIGURE 10. Leach Rate of Spent Fuels Based on Release of $^{239+240}\text{Pu}$ in Deionized Water at 25°C with Burnups of 9.0, 28.0 and 54.5 MWd/kgU

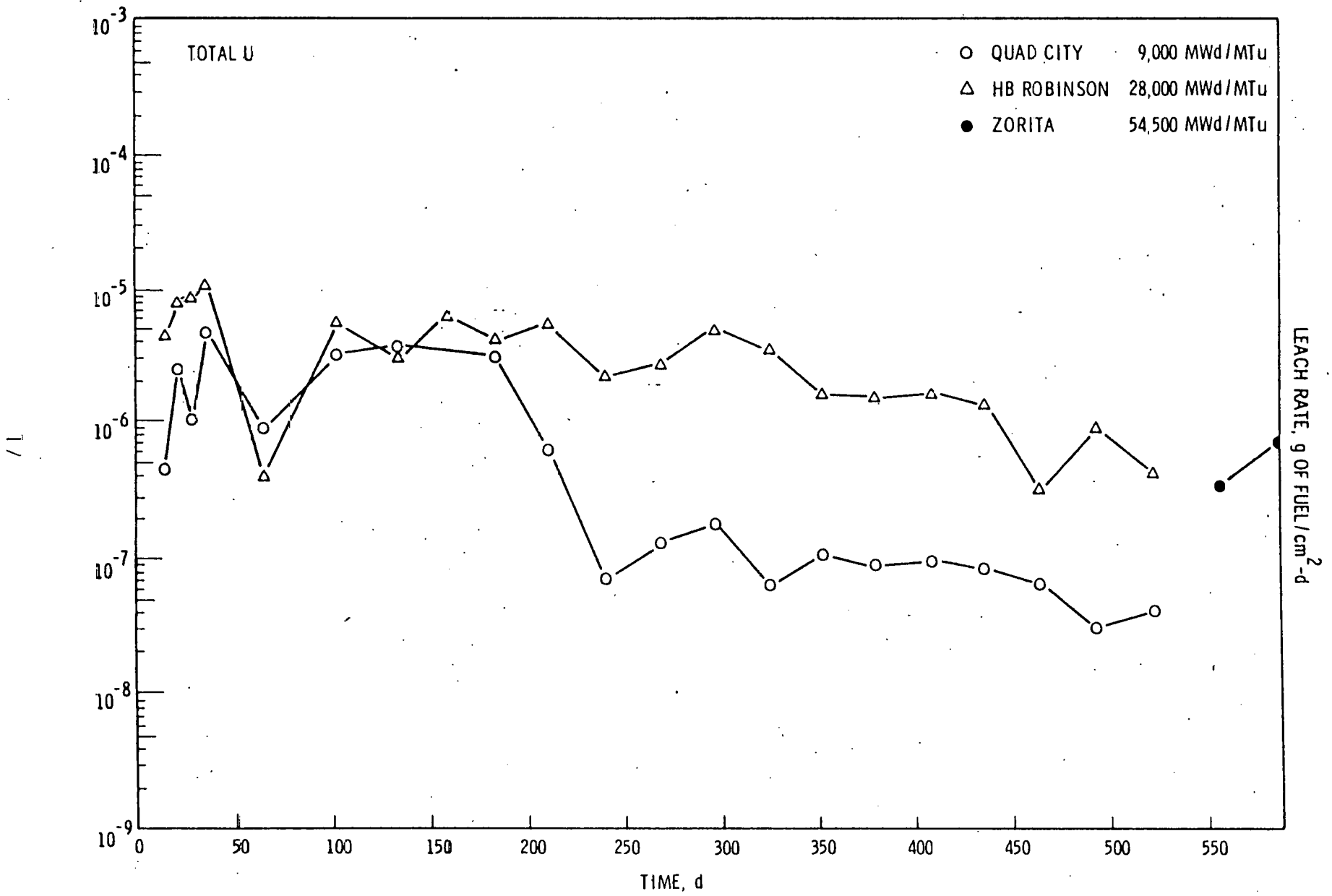


FIGURE 1. Leach Rate of Spent Fuels Based on the Release of Uranium in Deionized Water at 25°C

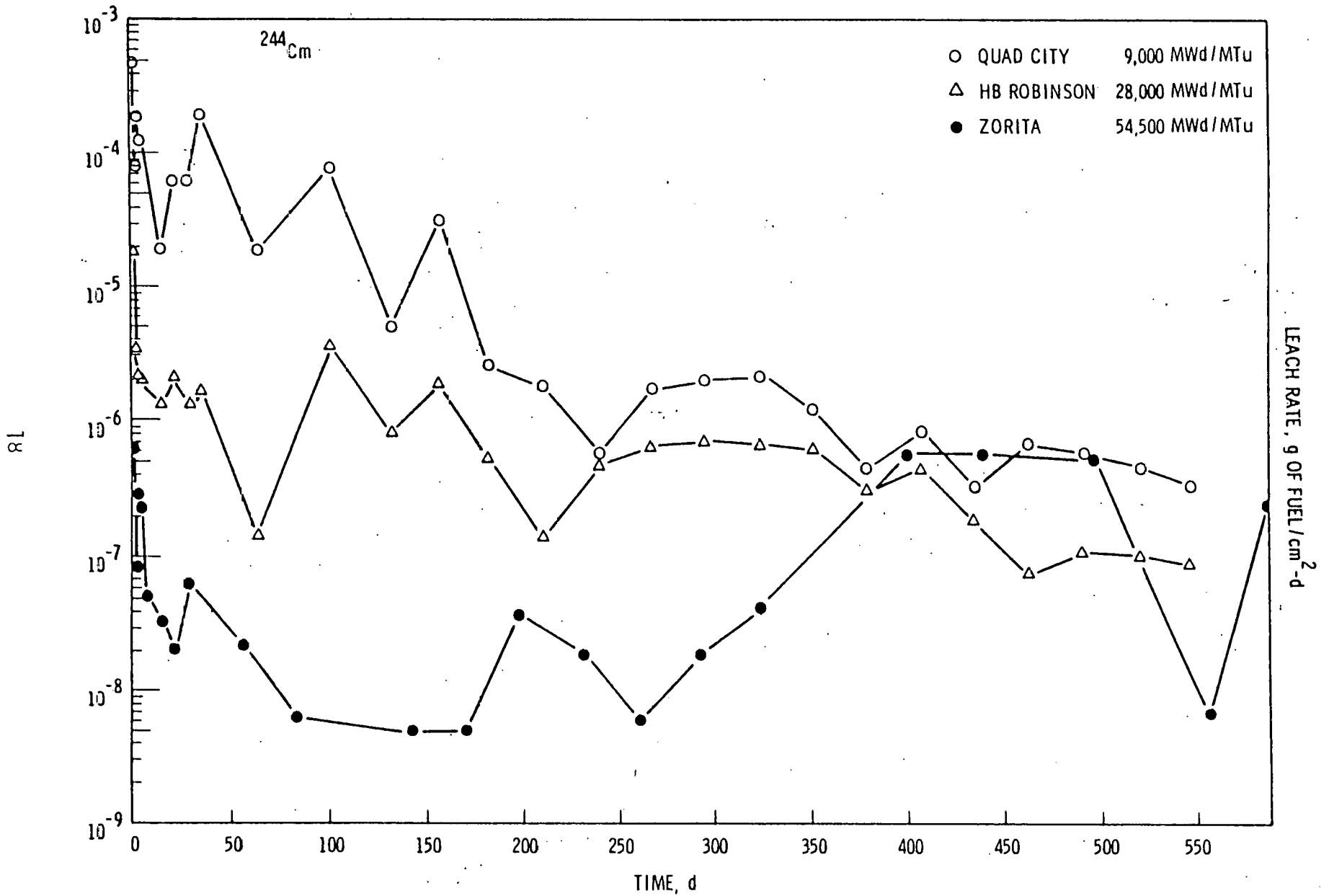


FIGURE 12. Leach Rate of Spent LWR Fuels Based on the Release of ^{244}Cm in Deionized Water at 25°C with Burnups of 9.0, 28.0 and 54.5 MWd/kgU

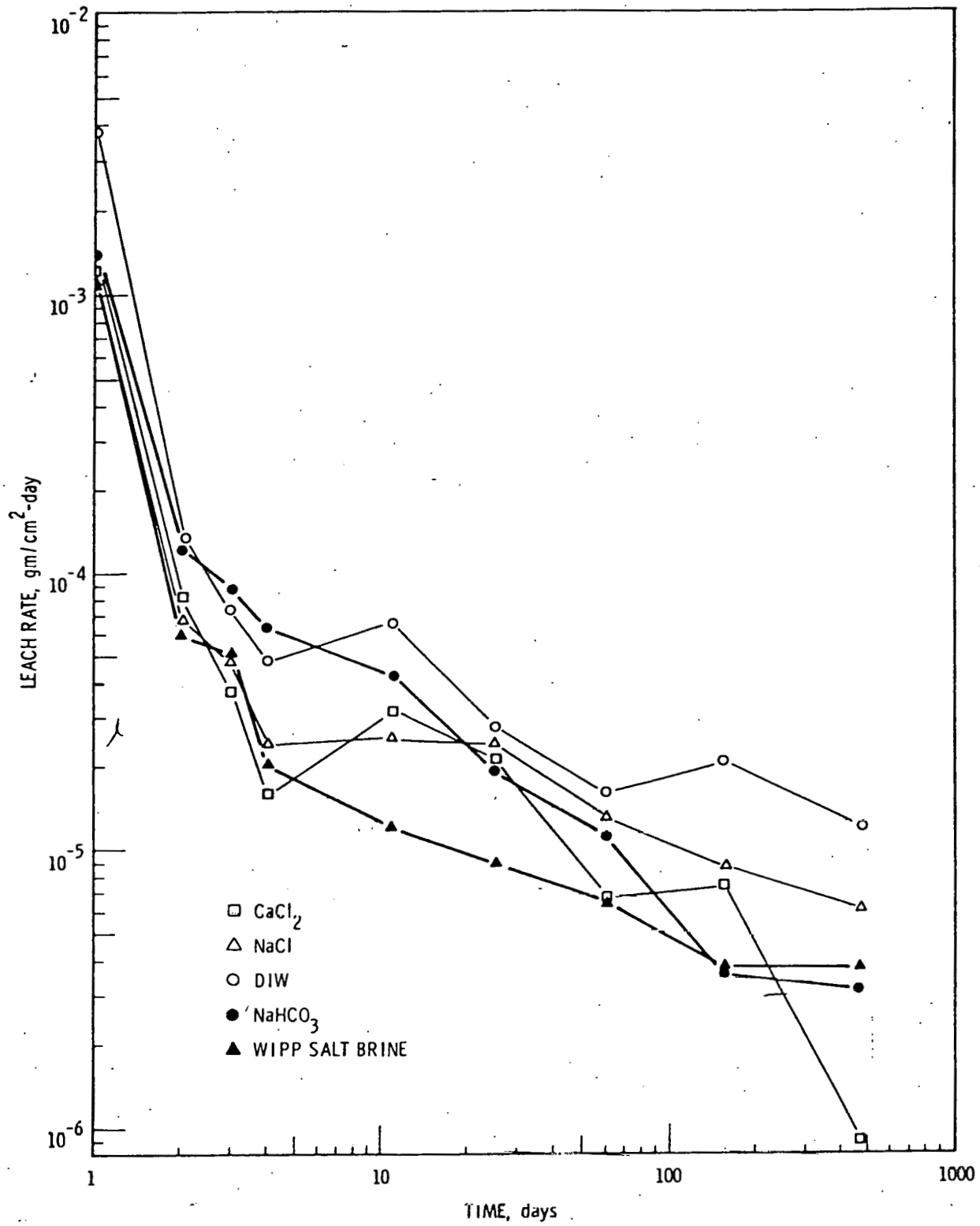


FIGURE 13. IAEA Leach Rate for 28 MWd/kg U Spent LWR Fuel at 25°C Based on Release of ¹³⁷Cs

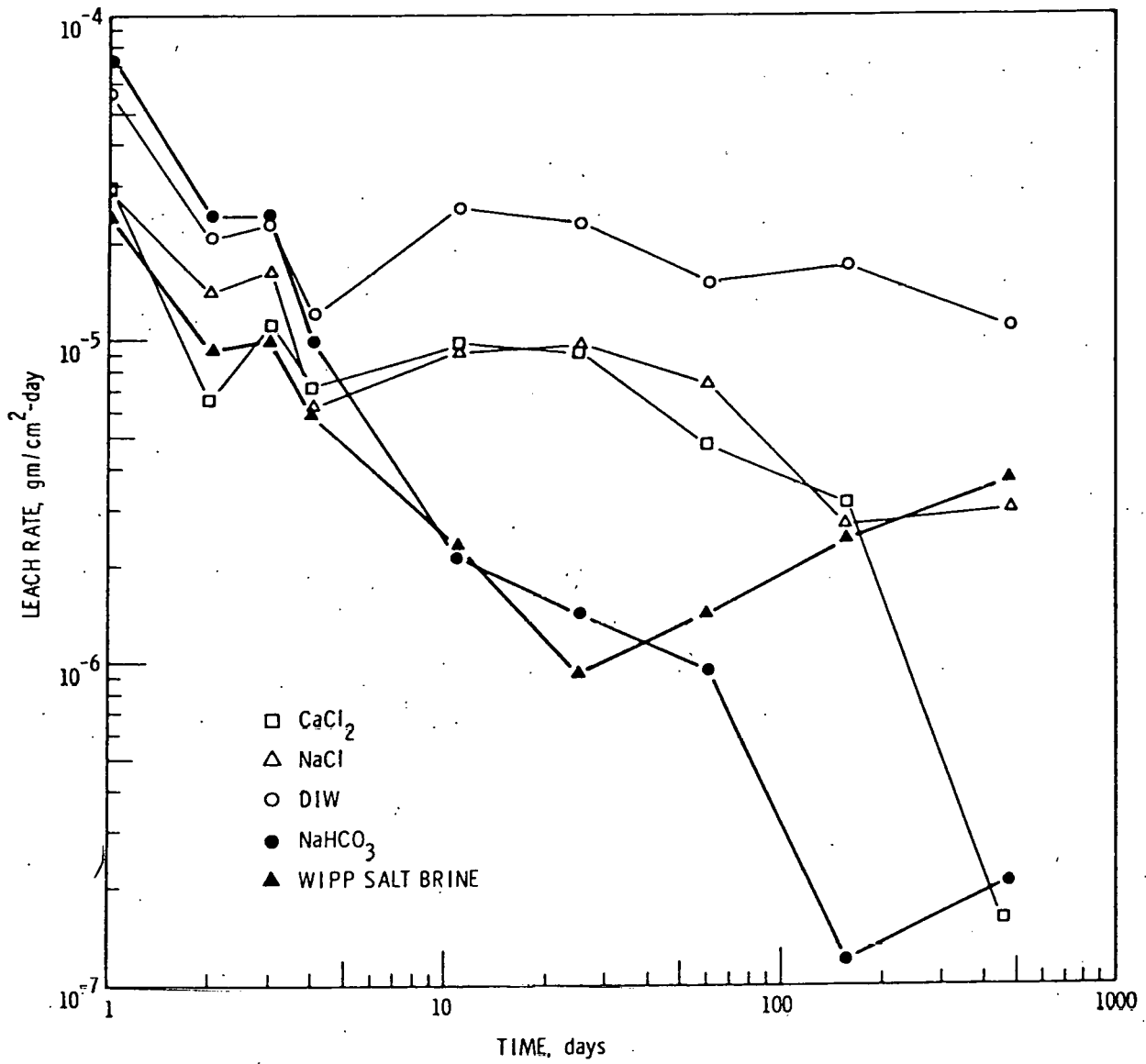


FIGURE 14. IAEA Leach Rate for 28 MWd/kg U LWR Fuel at 25°C Based on Release of ²³⁹+²⁴⁰Pu

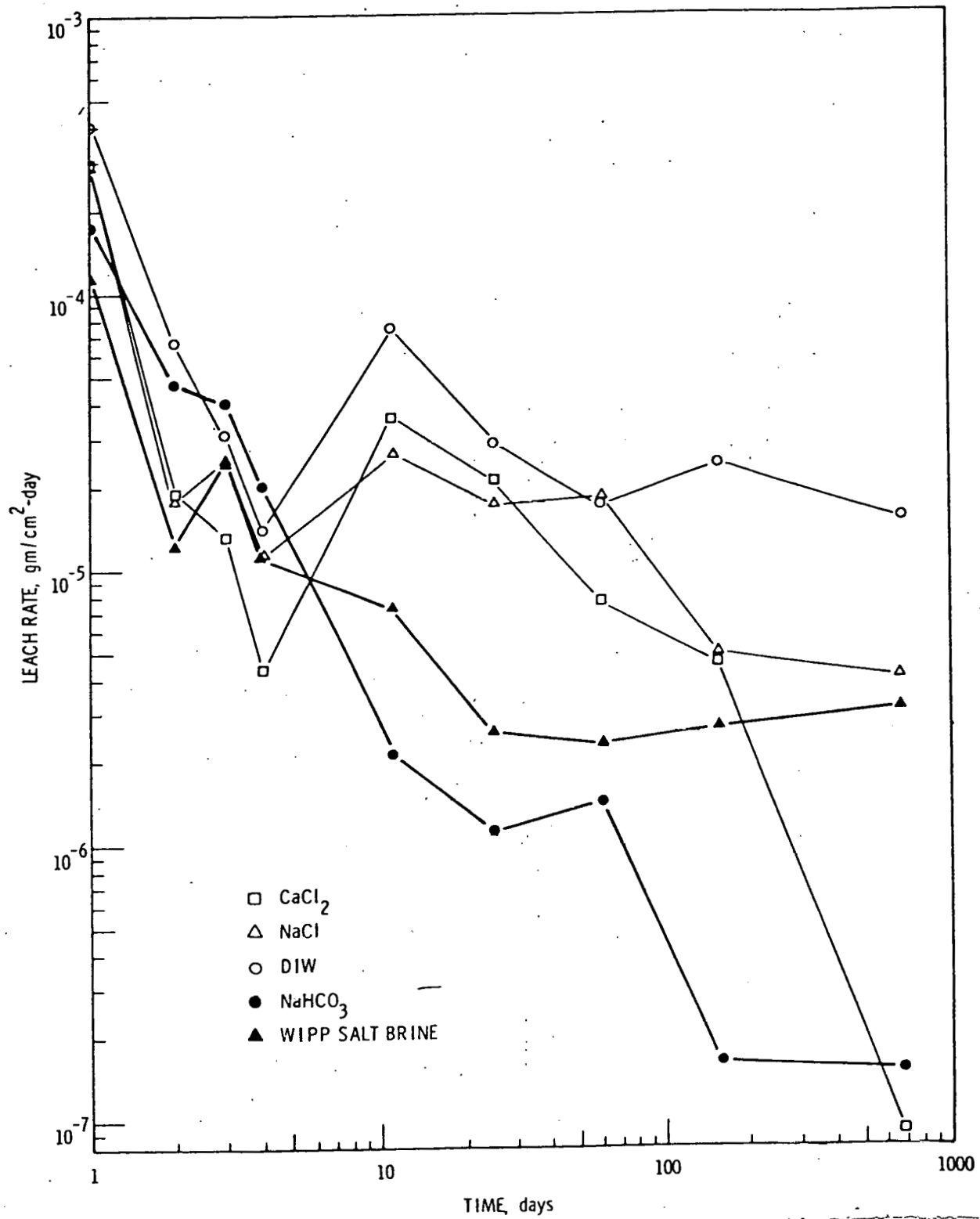
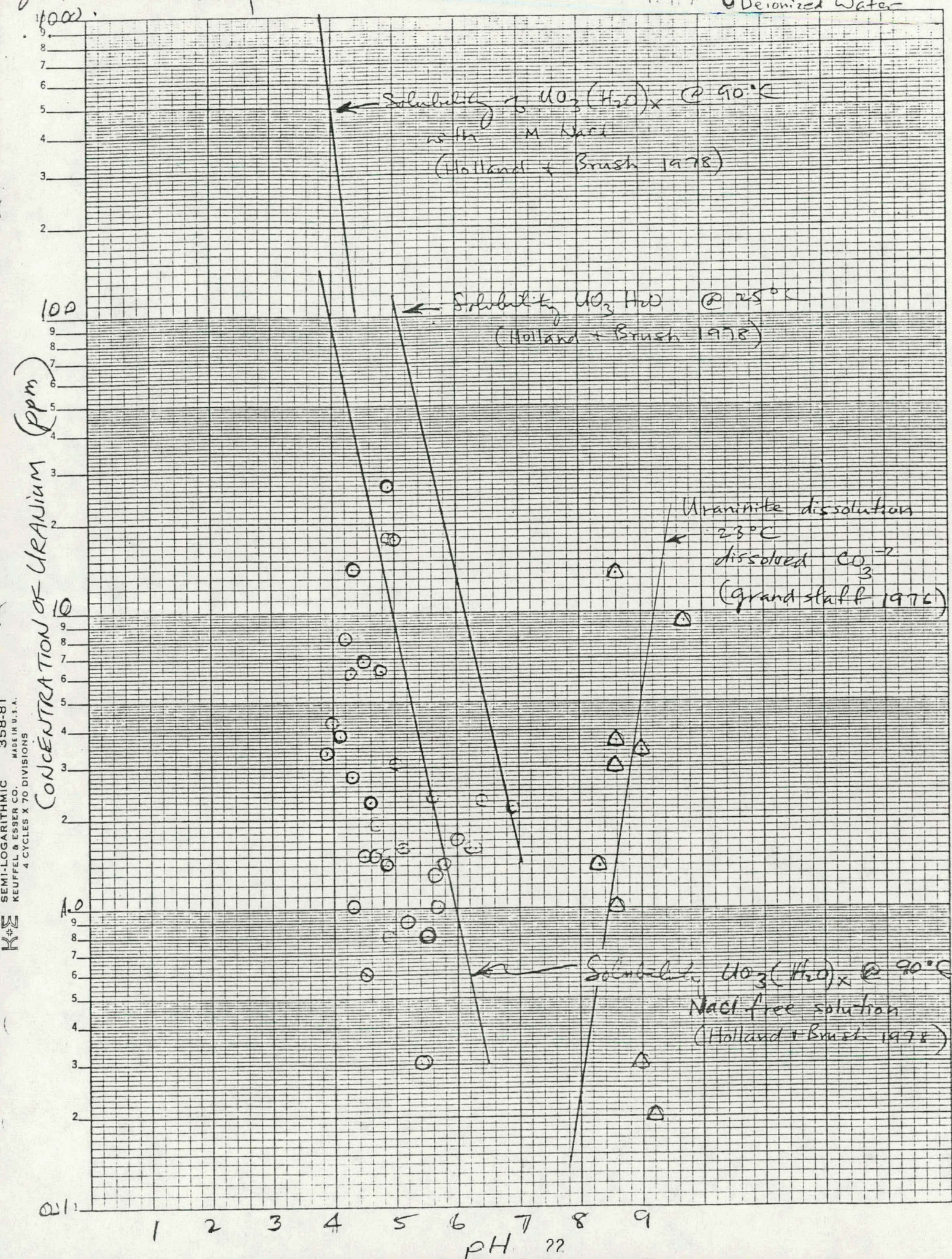


FIGURE 15. IAEA Leach Rate for 28 MWd/kg U LWR Fuel at 25°C Based on Release of ²⁴⁴Cm

Figure 16 Solubility of $UO_3(H_2O)_x$

○ CaCl₂ ○ NaCl △ NaHCO₃
 Deionized Water



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CONCLUSIONS

The spent fuel leach tests are ongoing. A few conclusions may be drawn from the progress of these tests.

The choice of leach test procedures may introduce differences in leach rate values (up to one order of magnitude between Paige procedure and IAEA procedure). Comparison of leach rates for spent fuels with burnups of 9, 28, and 54 MWd/kg U showed no discernible effect of burnup on leach rate. The leach rates are highest in deionized water (reference leachant) and lowest in 1.66 g/l CaCl_2 solution. Based on the release of plutonium and curium, spent fuel has a comparable leach rate to 76-68 glass in sodium bicarbonate solution and is two to three orders of magnitude less durable than 76-68 glass in deionized water and WIPP B brine solution.

Studies are underway at PNL to determine the release mechanism of radionuclides from spent fuels in various leach solutions.

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