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Leaching of Irradiated Light-Water-Reactor Fuel in a Simulated Post-Accident Environment

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J. H. Goode
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CHEMICAL TECHNOLOGY DIVISION

LEACHING OF IRRADIATED LIGHT-WATER-REACTOR FUEL IN A SIMULATED
POST-ACCIDENT ENVIRONMENT

A. D. Mitchell
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ABSTRACT

Personnel involved in cleanup operations following a light-water-reactor accident in which the fuel has been significantly damaged will have to consider the fission products that have leached from the fuel into the reactor water. In the study reported here, five samples of de-clad, irradiated fuel were leached in a borate solution that should approximate the post-accident conditions in a reactor. The resulting release of fission products was measured over the course of 1 year. The radioactivity levels of the leaching solutions were converted into leach rates and fractional releases. Fractional releases are projected for 4 years following the start of leaching. These values can be used to estimate the radioactive content of the reactor water before cleanup operations begin.

1. INTRODUCTION

One of the legacies of a successfully terminated accident involving damaged fuel is a reactor vessel filled with a borate solution and exposed fuel elements. The constituents of the irradiated fuel will leach from the elements once the fuel is exposed to water. In this study, a series of experiments was performed in which samples of spent fuel were leached in order to estimate the radioactive content of the resulting solution in a reactor vessel. The information obtained from these tests should give a reasonable estimate of the fraction of the fission-product inventory that will be found in the reactor water when cleanup operations begin. This information should also be useful in work involving spent-fuel pools or other modes of long-term storage of spent fuel. It should be noted that these experiments do not account for the fission products released

when the fuel rod ruptures; this quantity can be estimated from other work.¹ In addition, the fuel in these experiments was not subjected to the high temperatures and steam oxidation that would occur prior to fuel-rod failure. Further, this work is not intended to examine the particular mechanisms involved in leaching. Instead, the methods used are intended to determine "how much" rather than "why."

Five fuel samples were leached for ~ 1 year in a $0.3 \text{ M H}_3\text{BO}_3$ -- 0.05 M NaOH solution with a pH of 8. The experiments were conducted at boiling and near-boiling ($\sim 85^\circ\text{C}$) temperatures for fuel fragments of 18-, 50-, and 200-mesh size. These parameters were chosen so as to roughly approximate the conditions in a post-accident reactor vessel and to show the influence of particle size and temperature.

As an experimental control, two sampling techniques were used. In one, the entire leachant was replaced by fresh leachant during sampling; in the other, only a fraction of the leachant was replaced. The two techniques provide different information about the progress of the leaching. The tests with solution replenishment should indicate the presence of a solubility limitation or an autocatalytic effect that would not be detected by the tests with solution replacement. However, the tests with solution replacement give a much more sensitive indication of leaching rate.

When the experiments were terminated, a portion of the fuel fragments was dissolved to confirm the fission-product inventory.

2. PREVIOUS WORK

Previous leaching tests performed with spent fuel were primarily concerned with the leachability of unprocessed fuel in a nuclear-waste-repository environment. Generally, these were done with ground-water, deionized water, or brine as the leachant. In contrast, the present experiments were designed to investigate leaching in a reactor-vessel environment and used a borate solution as the leachant.

In experiments carried out at 25°C, Katayama leached de-clad fuel fragments in deionized water, distilled water, groundwater, and a synthetic sea brine.^{2,3} His results indicated that the relative speed of leaching is: Cs > Sb > Sr, Y > Pu > Cm. Further, they demonstrated that fuel burnup did not significantly alter the leaching rate, and that the use of brine or groundwater slowed the leaching rate. The long-term data were fit to the equation

$$F = Bt^m, \quad (1)$$

where

- F = total fraction of the substance released from the initial fuel,
- B = constant,
- t = time (d),
- m = exponent.

Using this equation, it was found that $m = 0.07$ for groundwater, $m = 0.31$ for deionized water, and $0.06 \leq m \leq 0.35$ for distilled water. The wide range for the distilled water was attributed to the varying quality of the building distilled water. Katayama also found that a period of accelerated leaching begins after about 600 d, possibly because of the breakdown of the fuel-fragment structure.

Strathdee et al. performed leaching tests with irradiated CANDU fuel.⁴ Sections of fuel rods were leached without removing the Zircaloy cladding. At 22°C the relative leaching rate with air-saturated distilled water and tap water was: $^{137}\text{Cs} > ^{90}\text{Sr} > ^{144}\text{Ce} > \text{Pu}$. Although the experiment was continued past 600 d, no accelerated leaching period was noted. Another segment of fuel was autoclaved at 150°C in distilled water without oxygen present. The ^{137}Cs leaching rate increased by an order of magnitude, but the ^{90}Sr rate decreased with respect to the previous test.

Norris and Bryant conducted leaching experiments with particular emphasis on waste isolation studies as related to the degree of containment found at the Oklo natural reactor.⁵⁻⁷ The experiments used 0.635-cm (0.25-in.)-thick slices of clad fuel from the H. B. Robinson

reactor. The leaching environment was carefully kept under reducing or oxidizing conditions by bubbling hydrogen or oxygen through the solution. At 25°C the leaching rate was slower in the reducing environment, with the exception of cesium, which was not affected. After 65 d the temperature was increased to 70°C. The results showed that the differences between the leaching rates in oxidizing and reducing conditions became negligible within the following 30 d. Additional data were taken to determine the dissolution rate for UO₂. The dissolution rate was found to be slower in a reducing environment and reasonably independent of temperature.

3. APPARATUS

We used very simple equipment for the leaching tests. The fuel and the leachant were put into standard 250-mL glass bottles. The bottles were then placed on electric hot plates to keep the solutions at the desired temperature. Water-cooled glass condensers were used to reflux the vapor. Teflon sleeves were positioned between the bottle and the condenser to seal the joint. (Fuel particles would have adhered to the joint if grease had been used for the seal.)

4. PROCEDURE

4.1 Preparation of Fuel Samples

The fuel used in these tests was a portion of fuel rod No. 32-028 from Oconee-1, end of cycle 2. The fuel was discharged on February 10, 1975, at an approximate burnup of 23,000 MWd/MTU. Table 1 gives the concentrations of the species examined in these tests.

The rod was sheared into 1.3-cm (1/2-in.)-long segments, and the fuel was dislodged from the cladding, coarsely crushed, and sieved. The three size fractions used in these experiments were the fractions retained by the 18-, 50-, and 200-size mesh (between 14 and 18 mesh, between 18 and 50 mesh, and between 100 and 200 mesh).

Table 1. Inventory of species present per gram of Oconee-1 fuel

Uranium, g	0.8603
Pu, counts/min	1.84E9
Gross alpha, counts/min	3.09E9
⁹ H, Bq	7.06E6
⁹⁰ Sr, Bq	1.27E9
¹⁰⁶ Ru, Bq	1.12E9
¹²⁵ Sb, Bq	6.1E7
¹²⁹ I, μ g	87.0
¹³⁴ Cs, Bq	7.87E8
¹³⁷ Cs, Bq	2.01E9
¹⁴⁴ Ce, Bq	1.40E9
¹⁵⁴ Eu, Bq	7.65E7

4.2 Preparation of the Leach Solutions

The leaching solutions were prepared by dissolving reagent-grade chemicals in twice-distilled water. To obtain the desired final concentrations of 0.30 M H₃BO₃ and 0.04 M NaOH, the required amounts of crystals were weighed and dissolved. Analysis of the solutions showed 3270 \pm 40 ppm boron as H₃BO₃ and 1050 \pm 90 ppm sodium as NaOH; the pH was 8.01 \pm 0.09. The solutions were then stored in plastic jugs; care was taken to exclude CO₂ from the air space.

4.3 Leach Tests with Solution Replacement

Two samples (\sim 10 g) of each of the 18- and 200-mesh fuel fragments were weighed and placed in separate 250-mL leaching bottles. Each bottle was filled with 100 mL of the borate leaching solution. A condenser was attached to each bottle, and the solution was heated to the desired temperature — one sample of each size at \sim 100°C and one of each size at 85 \pm 3°C. The temperature was monitored daily with a thermocouple, and the hot plate was adjusted as required. The water flowing through the condenser was sufficient to keep the system under total reflux.

To sample the leachant, the hot plates were turned off, and the solutions were allowed to cool and settle for about 1 h. The liquid was decanted and replaced with 100 mL of fresh leaching solution (at ambient temperature). The hot plates were then turned on, and the temperature was adjusted as required.

The leachant was either centrifuged (as in the first eight sets of samples) or allowed to settle further before samples were taken. Two 30-mL samples were decanted into plastic bottles. One bottle was submitted for analysis; the other was saved to check any questionable analytical results.

The solutions were gamma-scanned for most of the fission-product analyses. The presence of iodine was determined by activation analysis. The uranium concentration was determined by fluorescence, and the gross alpha activity was measured by direct counting. Analytical errors were generally reasonable. Table 2 shows typical errors as reported by the staff of the Analytical Chemistry Division. No error band was reported for the other constituents; however, there were several cases in which only one significant digit was reported for the uranium determination.

Table 2. Typical errors (in %) as reported by the Analytical Chemistry Division

^3H	2
^{106}Ru	33
^{125}Sb	18
^{129}I	7
^{144}Ce	32
^{154}Eu	37

The sampling frequency was similar to that recommended by Hesse.⁸ Samples were taken every working day for the first week, three times each week for the following 3 weeks, once each week for the subsequent 4 weeks, and about once each month thereafter.

4.4 Leach Tests with Solution Replenishment

After about three months, another experiment was started in which a portion of the leaching solution was replaced during sampling. The 50-mesh fuel fragments (~15 g) were placed in a 250-mL leaching bottle, and 150 mL of the solution was added. The condenser was fitted to the bottle, and the solution was heated to boiling.

The leachant was sampled as described in Sect. 4.3, but only ~30 mL of the solution was decanted. After further settling, two 10-mL samples were decanted from the 30-mL portion; the remainder was returned to the leaching bottle. Fresh borate solution was added to return the leaching solution to its original 150-mL volume. Samples were taken about once each month.

4.5 Termination of the Experiments

After the leaching study had been completed, the residual fuel fragments were stored for later use. Each fuel sample was dried with acetone and separated into two fractions. The first fraction was put in a capped bottle for storage, while the second fraction was dissolved in nitric acid so that an analysis of the remaining fuel and fission products could be made.

5. PRESENTATION OF RESULTS

Four trials, 85-18,* 85-200, 100-18, and 100-200, were made in which solution replacement was used for the sampling method and the leach rate was measured over discrete time intervals. One trial, 100-50, was made in which solution replenishment was used as the sampling method and the cumulative amount of material leached was determined.

*The two numbers in these designations refer to temperature and sieve size, respectively.

5.1 Leach Rates

The equation used by Katayama² was chosen for calculating leaching rates for all trials except 100-50. The equation is as follows:

$$R_i = x_i M / [x_o A (t_i - t_{i-1})] , \quad (2)$$

where

- R_i = leach rate (g of fuel leached/d·cm²),
- x_i = amount of a particular species found in the leach solution i ,
- x_o = amount of a particular species in the original fuel sample,
- M = mass of the fuel sample (g),
- A = surface area of the fuel sample (cm²),
- t_i = leaching time up to when sample i was taken (d).

Trial 100-50 was used only as a comparison for the total fraction released.

It is important to note the particular units used in this form of the leach rate. Leach rates are often reported as the fraction of the inventory leached per unit of time. However, in this formulation, the rate is expressed as the fraction of the inventory leached per unit of time, divided by the surface area per gram of fuel.

Values for x_o (given in Table 1) were taken from analyses of the dissolved fuel after this series of experiments had been terminated and from analyses for previously dissolved fuel.^{9,10}

Values for the area, A , are only approximate. The area was calculated by considering the sieve dimensions and by making assumptions about the shape of the fragments. Photographs of the 18-mesh fuel were measured to obtain an independent estimate of the surface area. The results of these two methods were quite close, which shows the insensitivity of the area-per-mass ratio. However, these numbers should not be construed as being the actual surface area open to leaching since, as can be observed in the photographs, the surface is rough and uneven. The area is used only as a constant divisor that will, we hope, put the different sieve sizes on the same basis.

The duration of the leaching period is given by t_i , but the calculated rate from Eq. (2) is an average rate from t_{i-1} to t_i . Thus, the time

associated with the rate is the average of t_{i-1} and t_i . Because of repairs in the facility, there was a 2-week break in the experiment. For trial 100-50, the break occurred after 25 d of leaching, whereas, for 85-18, 85-100, 100-18, and 100-200, the break occurred after 102 d of leaching. Even though the fuel remained in the leachant during this interval (at ambient temperature), the 2-week break was neglected in determining the total days of leaching.

Because a significant amount of scatter was found in the experimental data, the data smoothing routine (3RSSH twice) described by Tukey was used.¹¹ Figure 1 is a typical example of the data before and after smoothing. The plots in all subsequent figures will display the data after smoothing unless otherwise noted.

Figure 2 gives the leach rates for uranium. These values are also a measurement of the fuel dissolution rate. We expect this rate to be reasonably constant since the leaching solution is always at essentially zero concentration in uranium. The rate, which was initially $\sim 10^{-6}$ g fuel/d \cdot cm², slowly decreased to $\sim 10^{-8}$ g/d \cdot cm². The decrease could be due to a reduction in the surface area open for dissolution, as suggested by Katayama,² or it could be caused by the formation of some type of passivating layer, as suggested by Strathdee et al.⁴ Such a decrease could also result if a solubility limit were reached during each sampling period. Because the amount leached is divided by progressively longer time periods, the resultant leaching rate would artificially decrease. However, the decrease in the rate cannot be attributed to a limiting solubility for UO₂ since the leaching solution was replaced before a limiting solubility was reached and the uranium concentration of the samples generally declined during the course of the experiment.

The curves in Fig. 2 suggest that the dissolution rate is slower at 100°C than at 85°C. Particle size seems to have no consistent effect on the long-term dissolution rate, but the short-term rate is higher for the larger particles (18 mesh). However, it should be noted that, in the tests with the larger fuel fragments, the uranium concentration in the leaching solution was very close to the limit of analytical

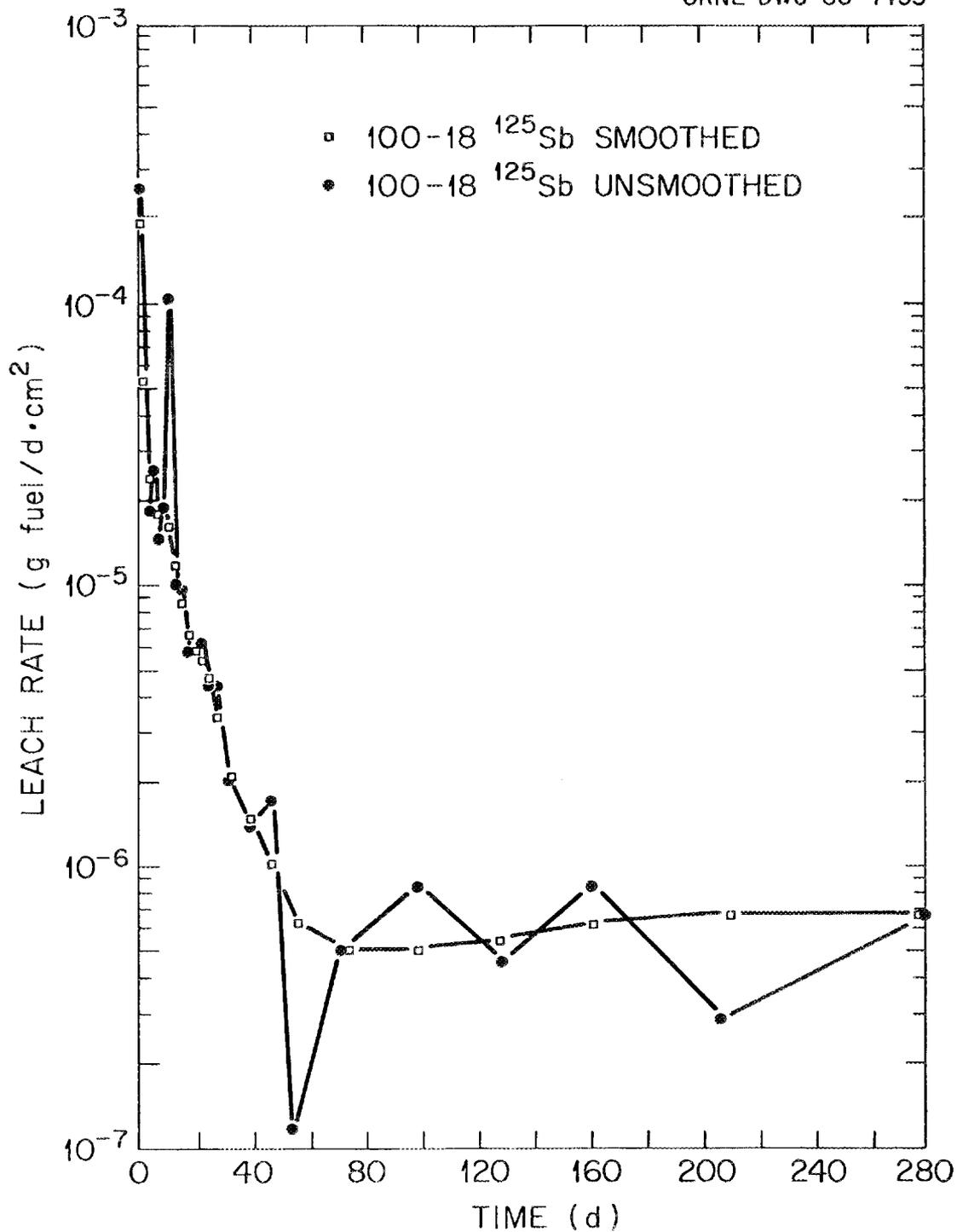


Fig. 1. Experimental data before and after smoothing.

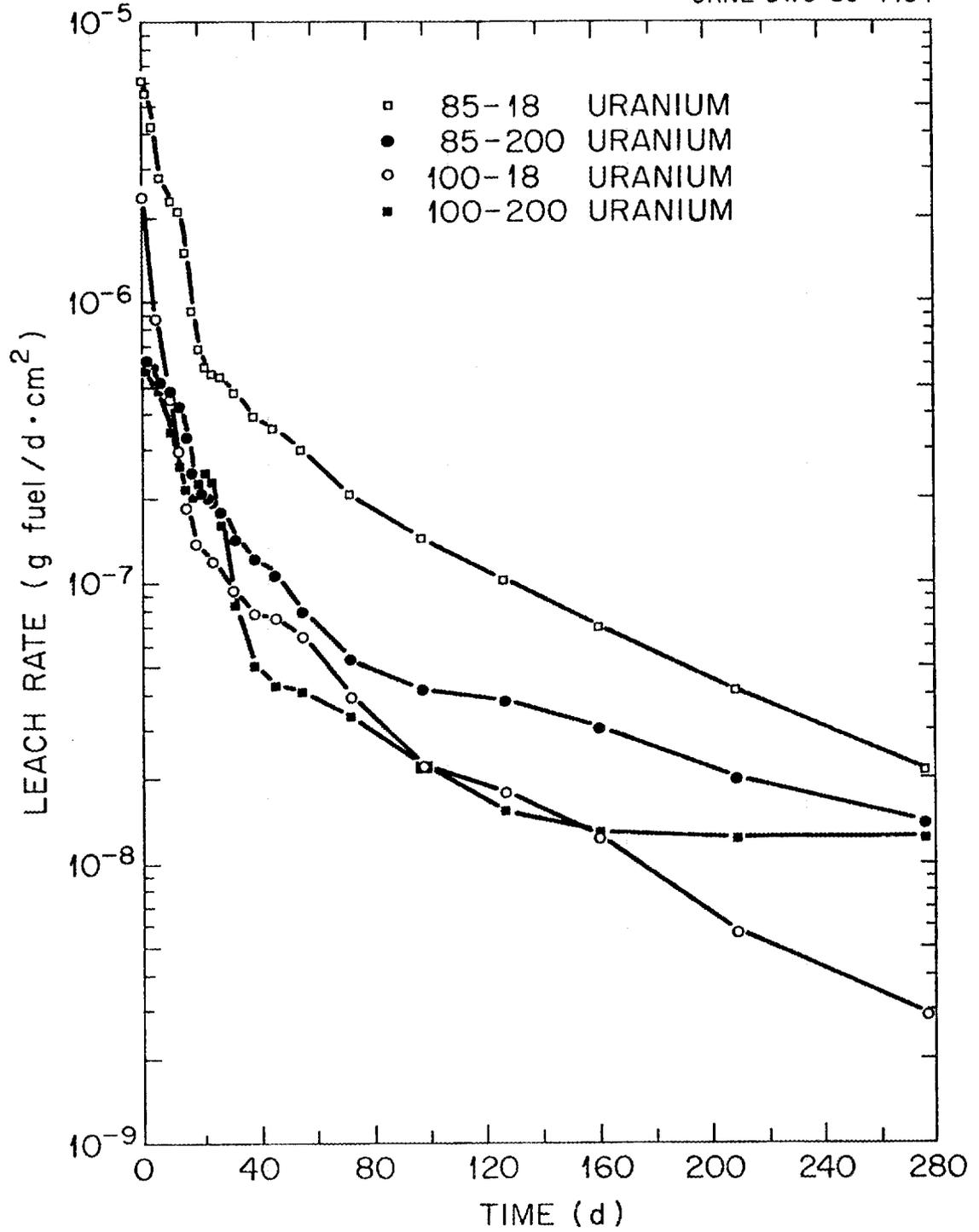


Fig. 2. Leach rates for uranium.

detection and that the results (especially for 100-18) are only known to one significant digit.

The leach rate for gross alpha activity was also measured; results are given in Fig. 3. This rate, which was initially $\sim 6 \times 10^{-7}$ g fuel/d \cdot cm², fell to $\sim 2 \times 10^{-9}$ g/d \cdot cm². This is substantially lower than the rate for uranium. No definite temperature effect was found; however, the small fragments have a higher long-term and a lower short-term leach rate.

Since cerium and europium (as fission products) do not segregate within the fuel matrix during irradiation, their leaching rate should be similar to that of the uranium matrix.¹² Figures 4 and 5 show the results for ¹⁴⁴Ce and ¹⁵⁴Eu, respectively. The curves are very similar to those for uranium, and some of the same features are apparent. The rate of leaching, which is initially $\sim 1 \times 10^{-6}$ g fuel/d \cdot cm², gradually decreases to $\sim 1 \times 10^{-8}$. The decrease is slightly more rapid for ¹⁴⁴Ce than for uranium, but the difference is probably within experimental error. Although there are not enough data points to determine the long-term influence of temperature and fragment size, the short-term rate for the larger particles is higher for both ¹⁴⁴Ce and ¹⁵⁴Eu. This was also the case for uranium.

In contrast to the rare earths, some fission products migrate within the fuel during irradiation and preferentially deposit in cracks and voids¹² — the primary example is cesium. The experimental data for ¹³⁴Cs and ¹³⁷Cs are shown in Figs. 6 and 7, respectively. As would be expected, these two isotopes replicate each other, as is seen in the corresponding curves. No effect of temperature is evident, but the large fragments release cesium at a higher rate than do the smaller particles. This effect seems to disappear in the long-term rates. Over the leaching period, the leach rate for cesium declines from $\sim 5 \times 10^{-5}$ g fuel/d \cdot cm² to $\sim 1 \times 10^{-7}$. The rate initially decreases very rapidly, which may be caused by the depletion of cesium in the cracks.

Iodine in irradiated fuel is suspected of being in the form of CsI; thus, the leach rates of cesium and iodine would be expected to be similar.¹² Figure 8 shows experimental data. Because of a sparsity of

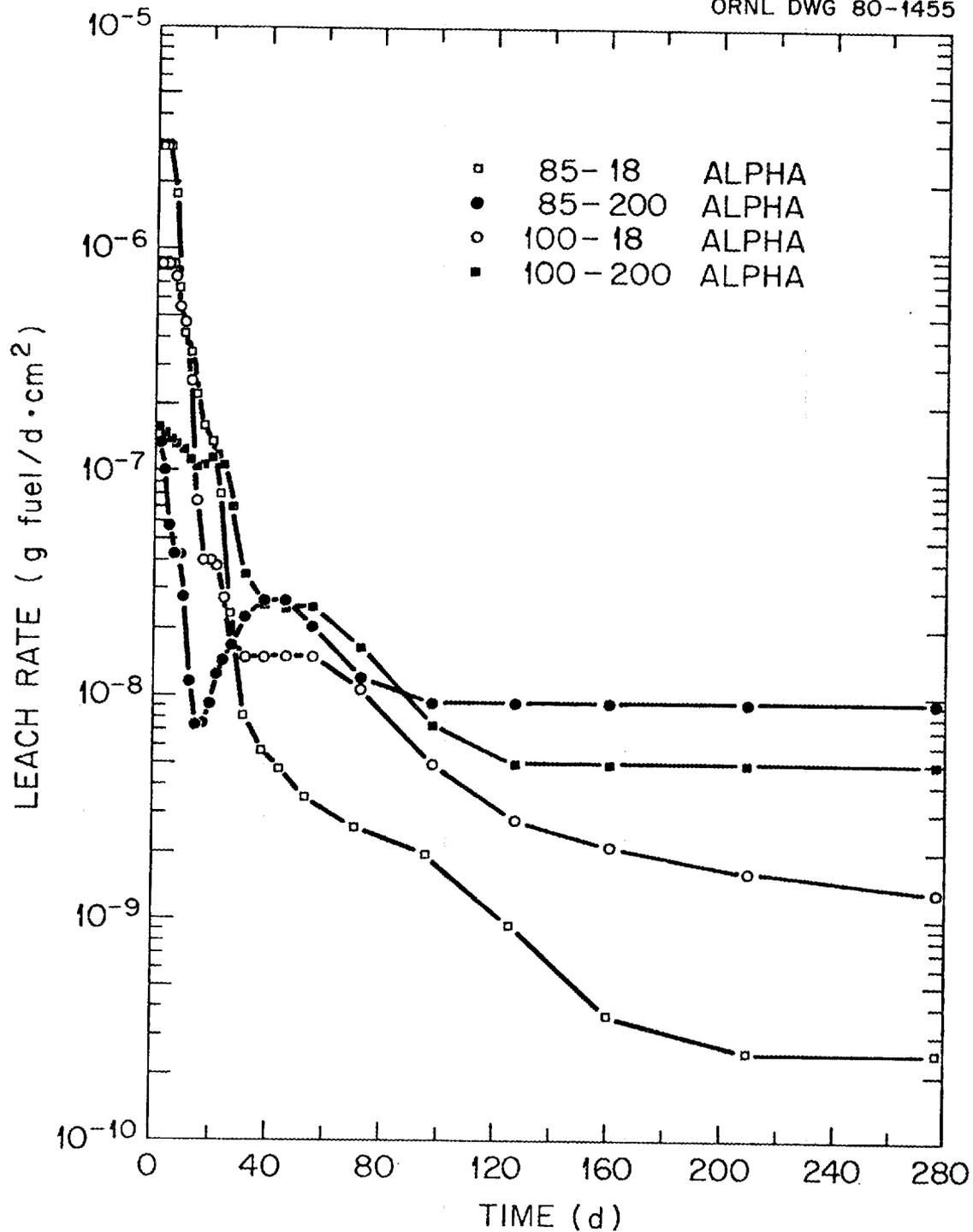


Fig. 3. Leach rates for gross alpha activity.

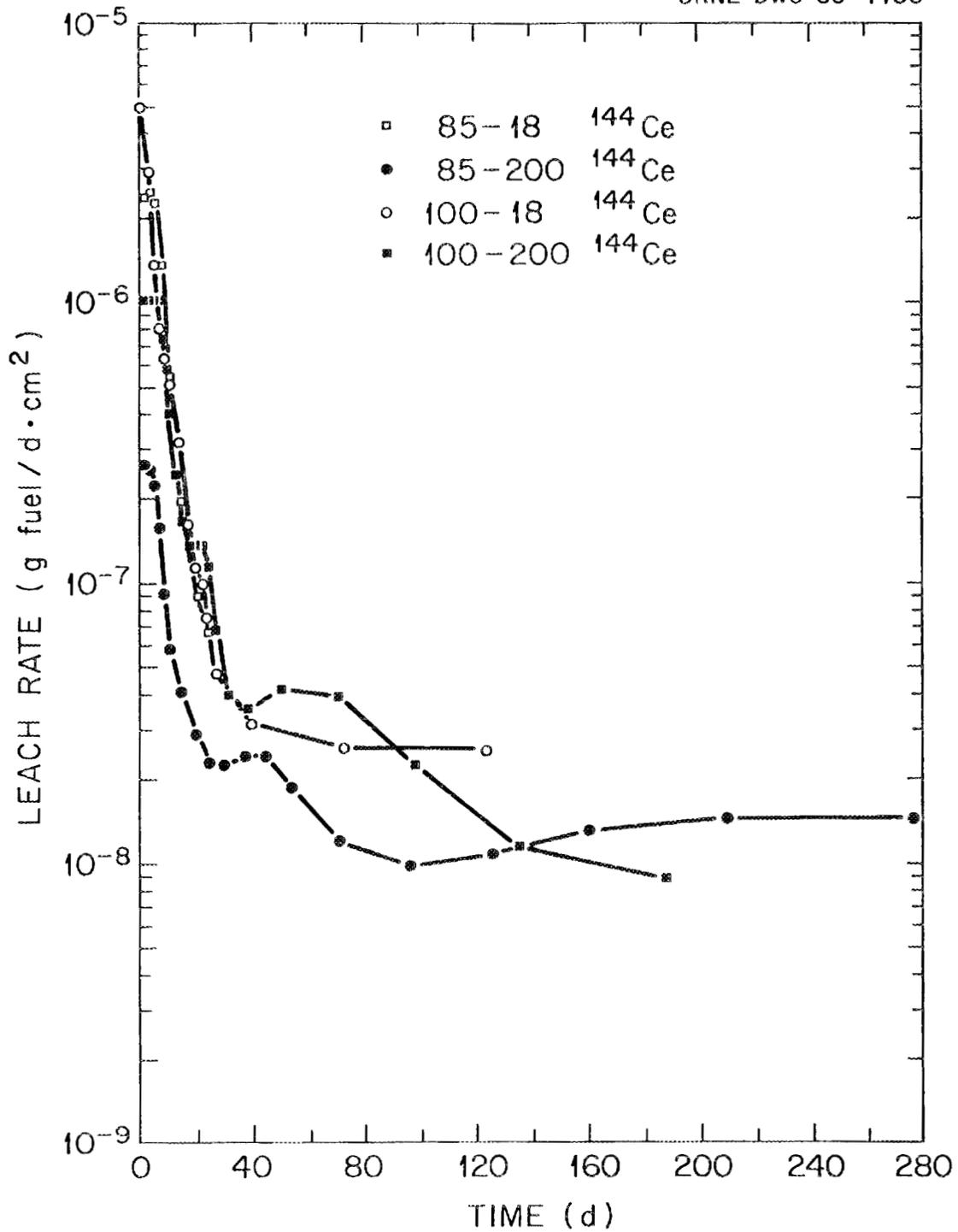


Fig. 4. Leach rates for ^{144}Ce .

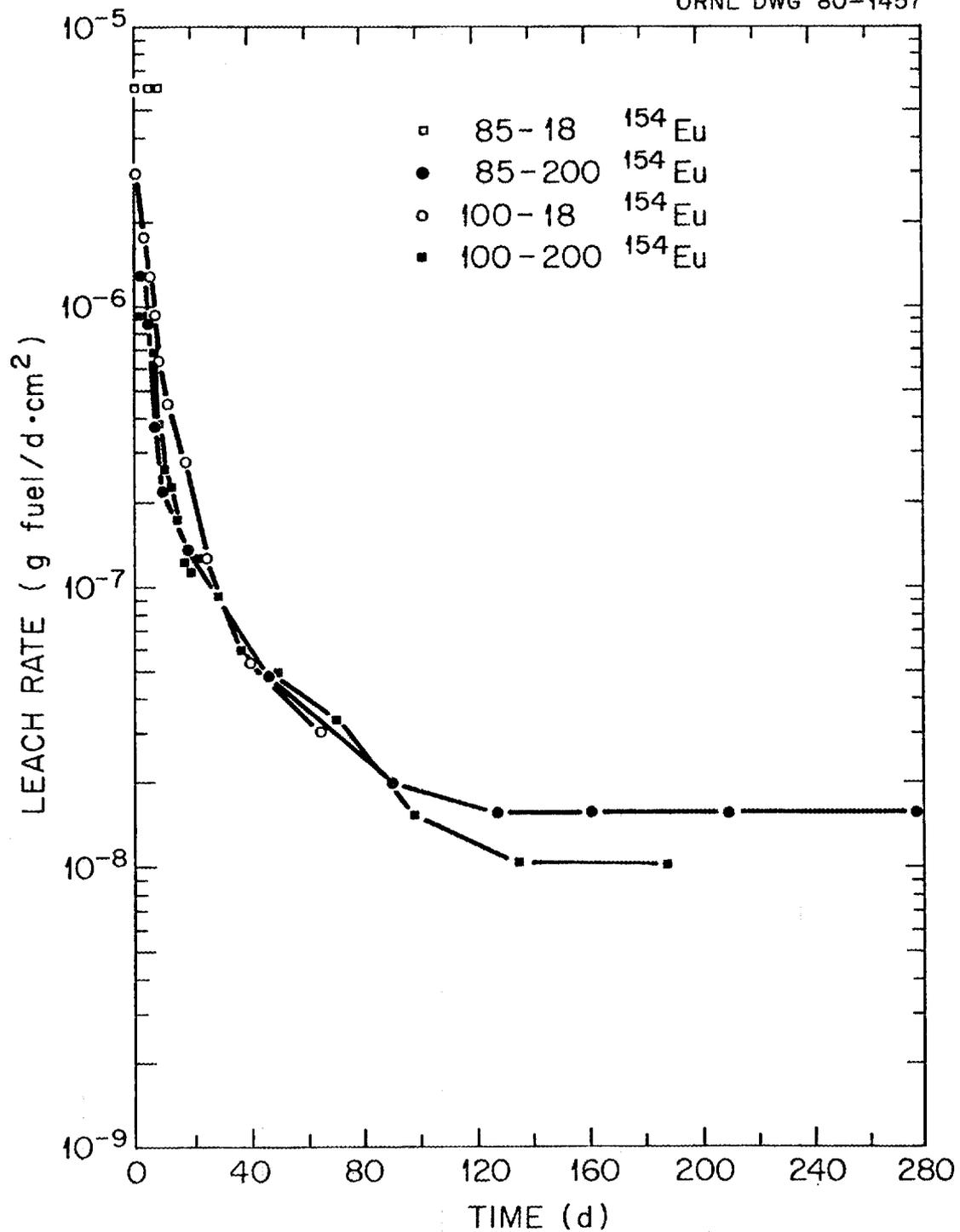


Fig. 5. Leach rates for ^{154}Eu .

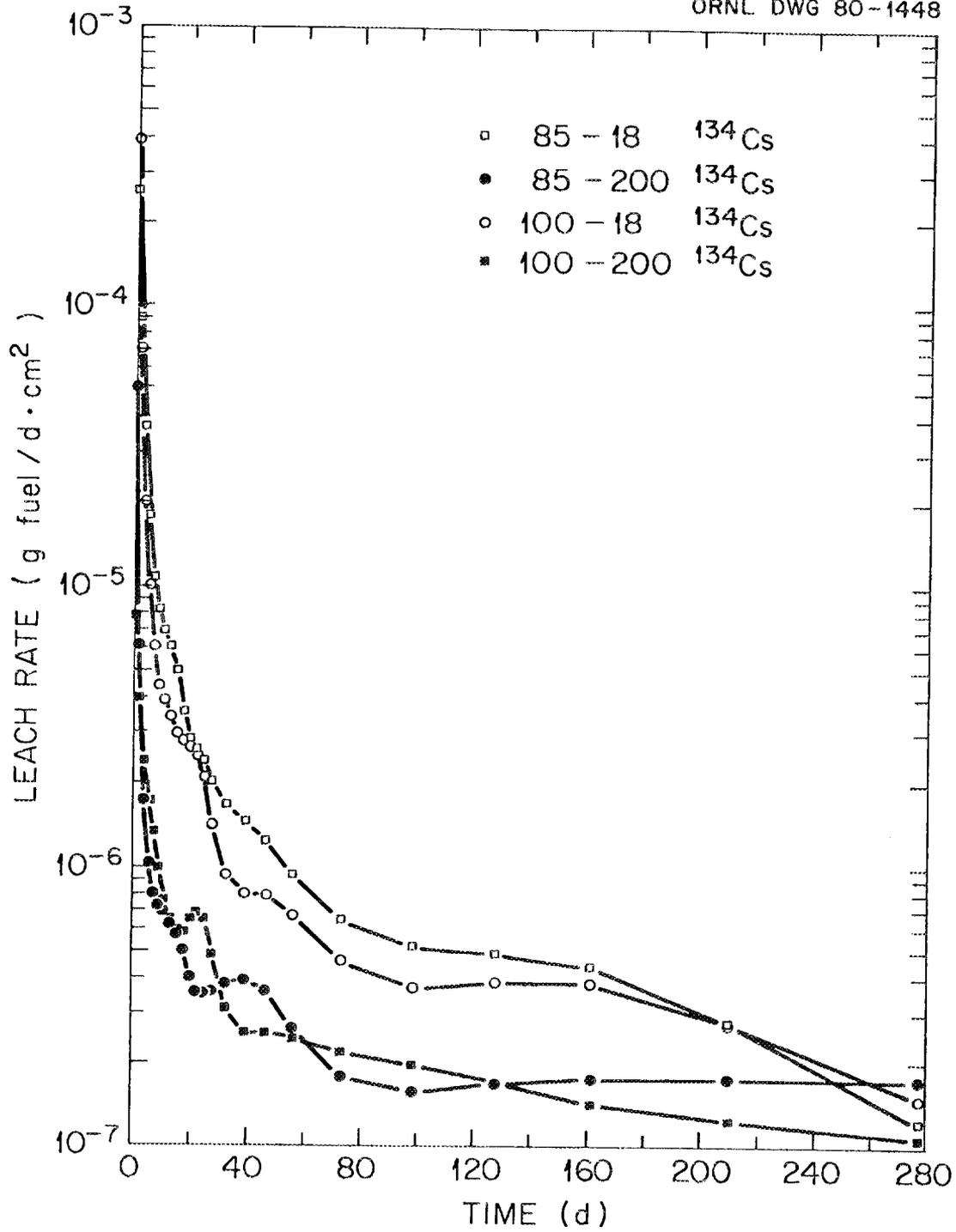


Fig. 6. Leach rates for ^{134}Cs .

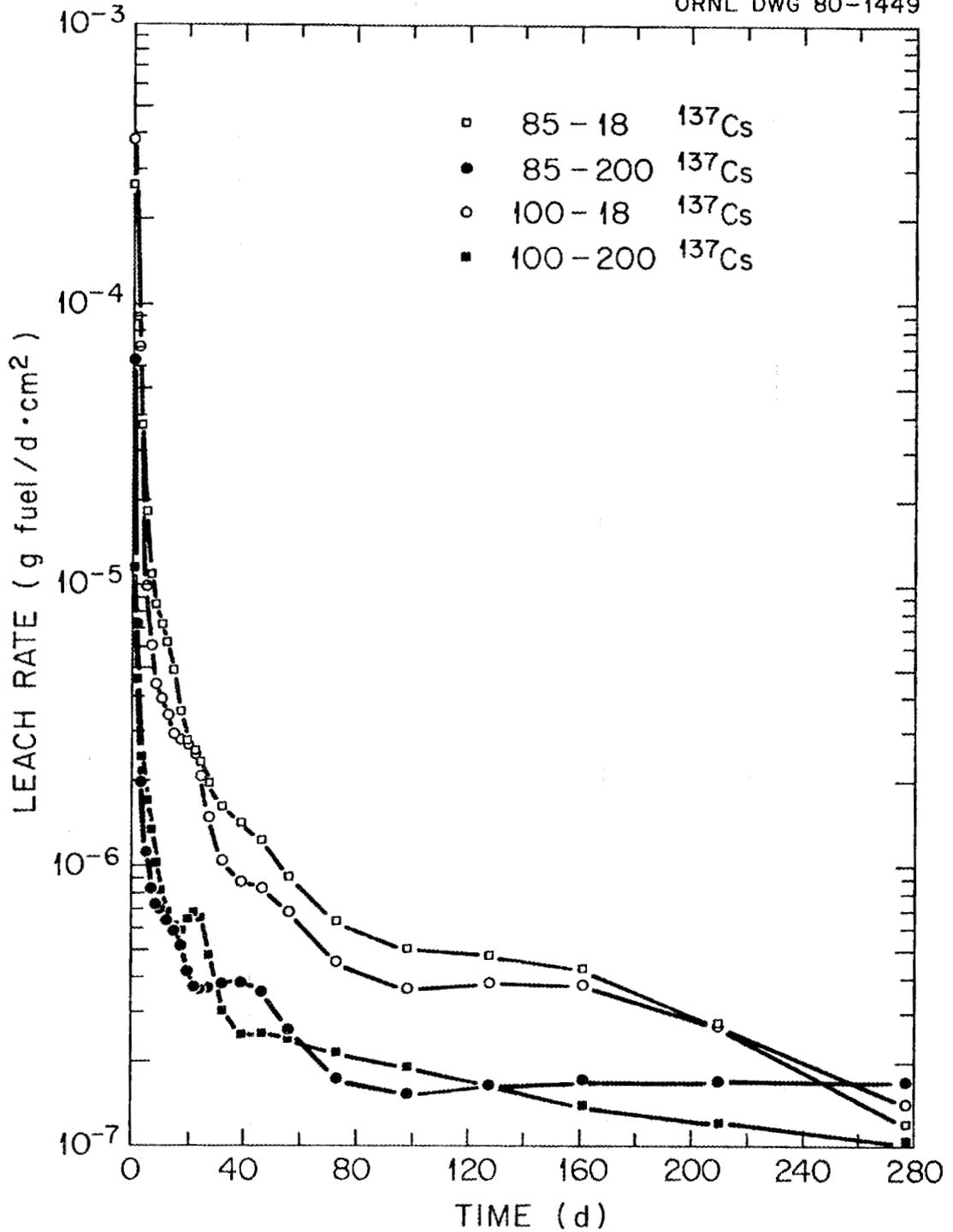


Fig. 7. Leach rates for ^{137}Cs .

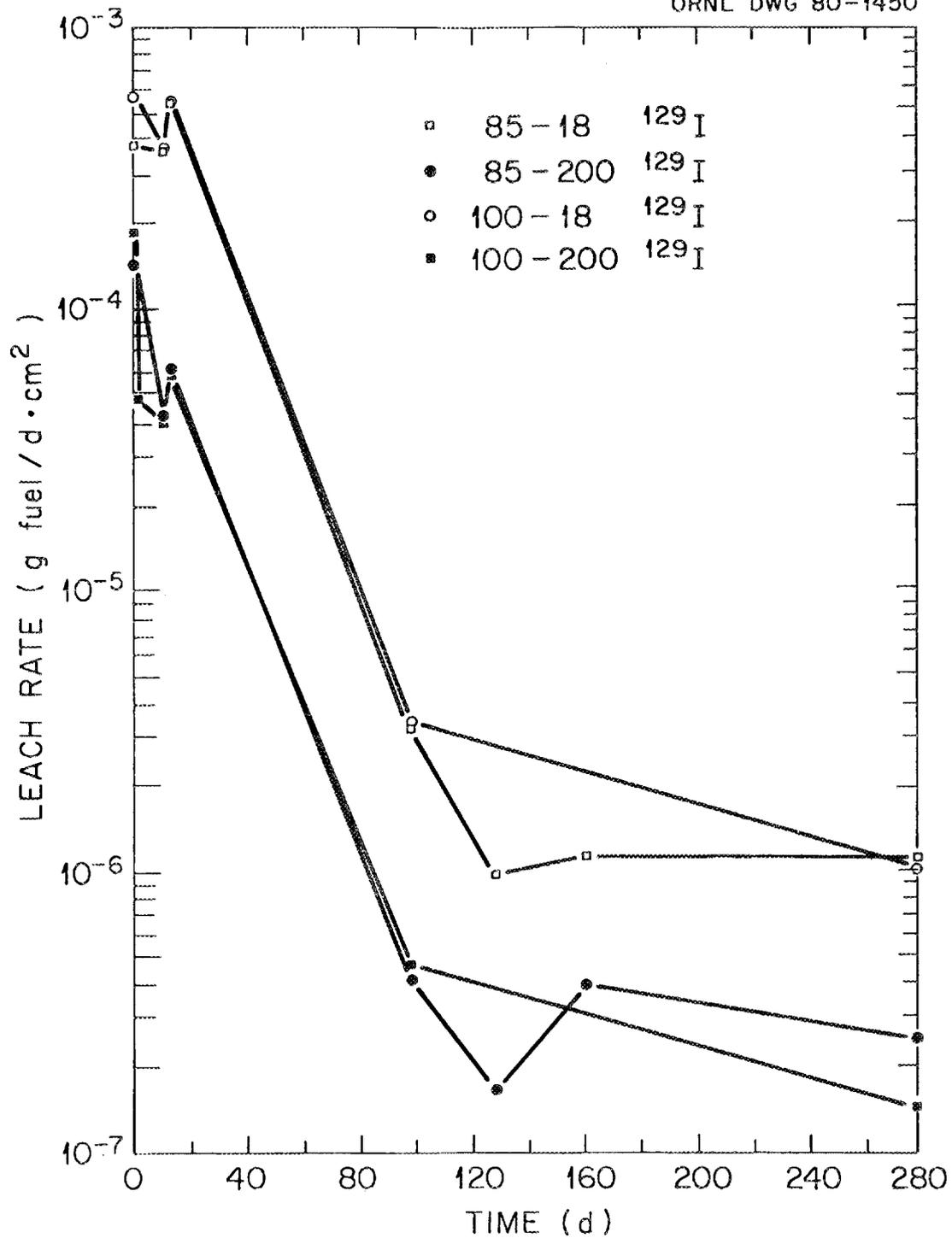


Fig. 8. Leach rates for ^{129}I .

points, the data are given in the original rather than the smoothed form. The initial leach rate is $\sim 3E-4$ g fuel/d \cdot cm 2 , whereas the final rate is $\sim 5E-7$ g/d \cdot cm 2 . These values are moderately higher than those measured for cesium, due to the larger cesium inventory that appears in the denominator of Eq. (2). If the values are in terms of μ mol/d \cdot cm 2 , as in Fig. 9, the leaching of CsI becomes more apparent. No definite effect of temperature is observed, but the iodine in the larger fuel fragments leaches at a higher rate.

The results for ^{125}Sb (see Fig. 10) are similar to those for cesium. The leaching rate, which is initially $\sim 5E-5$ g fuel/d \cdot cm 2 , decreases to $\sim 5E-7$ g/d \cdot cm 2 . The larger fuel pieces release antimony more quickly over the early time period. Although no definite temperature effect is apparent, the curves indicate that ^{125}Sb might leach faster at lower temperatures.

Figure 11 shows the results for ^{106}Ru . The leach rate starts at $\sim 2E-6$ g fuel/d \cdot cm 2 and decreases to $\sim 2E-8$ g/d \cdot cm 2 . The reduction in the leach rate is slightly more erratic than was seen in the other plots, which may be caused by the smoothing routine and erratic data or by the form that ruthenium takes in irradiated fuel. Ruthenium tends to concentrate in metallic inclusions in the fuel;¹² thus, the small peaks in Fig. 11 may be the result of leaching the fuel and periodically releasing some of these inclusions. No clear effect is seen for the temperature or the fuel-fragment size; again, however, the short-term leach rate is higher for the larger particles.

Figure 12 gives the results for ^{90}Sr . Strontium is leached from the larger particles at a higher rate, and the trials at 100°C generally show a higher rate than do those at 85°C. The initial leach rate is $\sim 5E-6$ g fuel/d \cdot cm 2 ; the final rate is $\sim 8E-8$ g/d \cdot cm 2 .

Figure 13 gives the results for tritium. The rate, which is initially between $7E-7$ and $5E-5$ g fuel/d \cdot cm 2 , declines by about an order of magnitude during the next two months and then levels off at $\sim 2E-7$ g fuel/d \cdot cm 2 . Although tests show no conclusive effect of temperature throughout the test, particle size appears to be significant. The large

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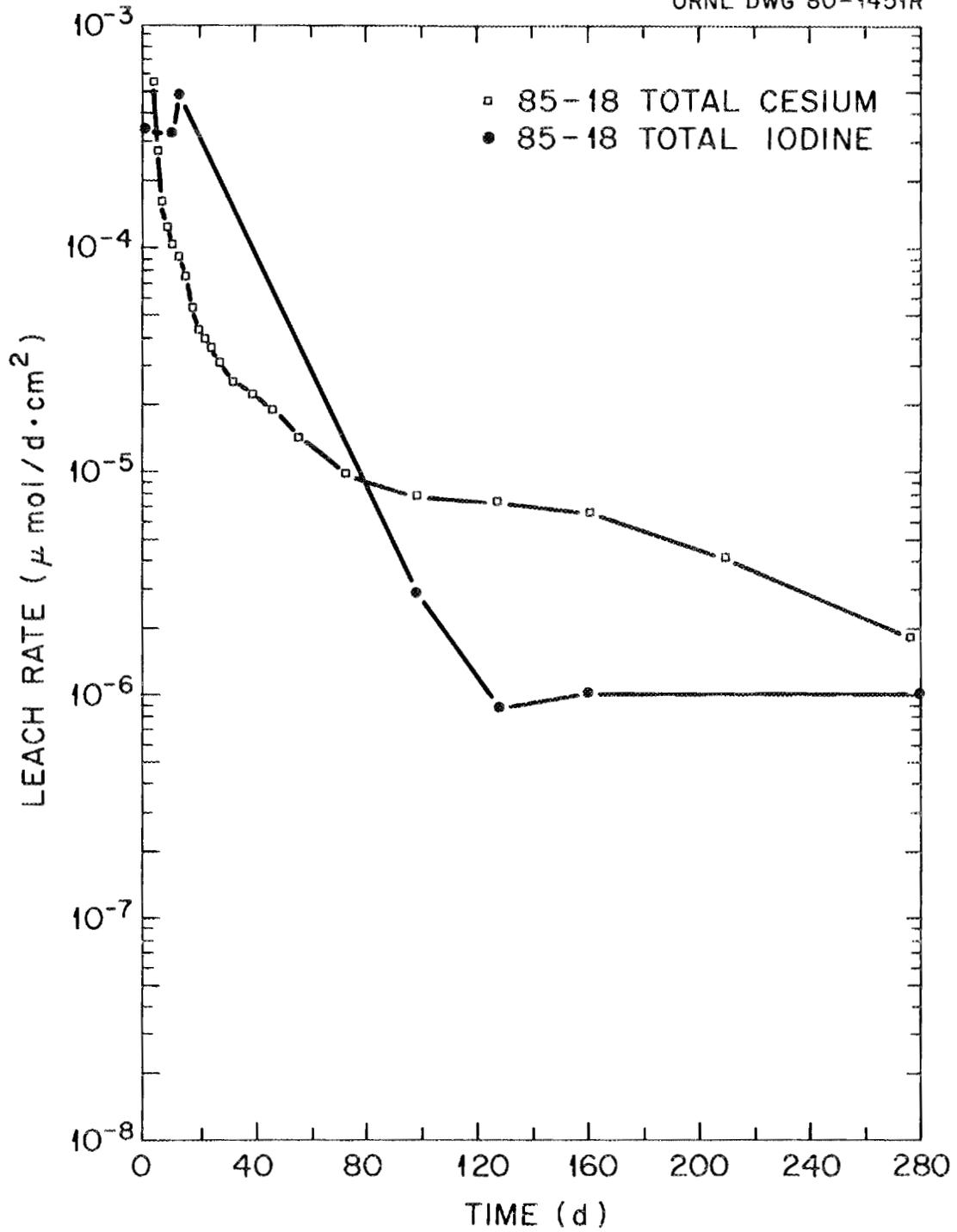


Fig. 9. Comparison of leach rates for total cesium and total iodine.

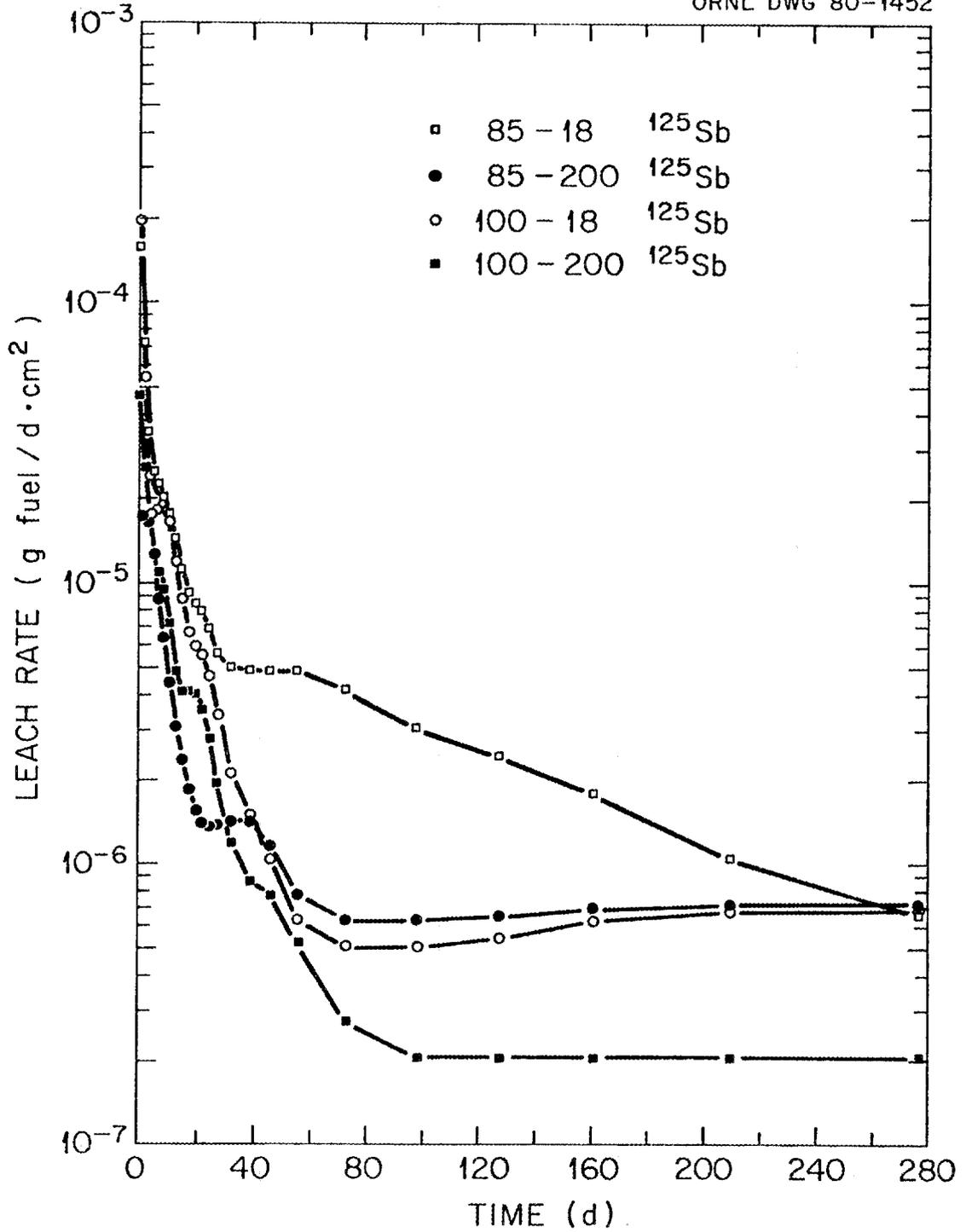


Fig. 10. Leach rates for ^{125}Sb .

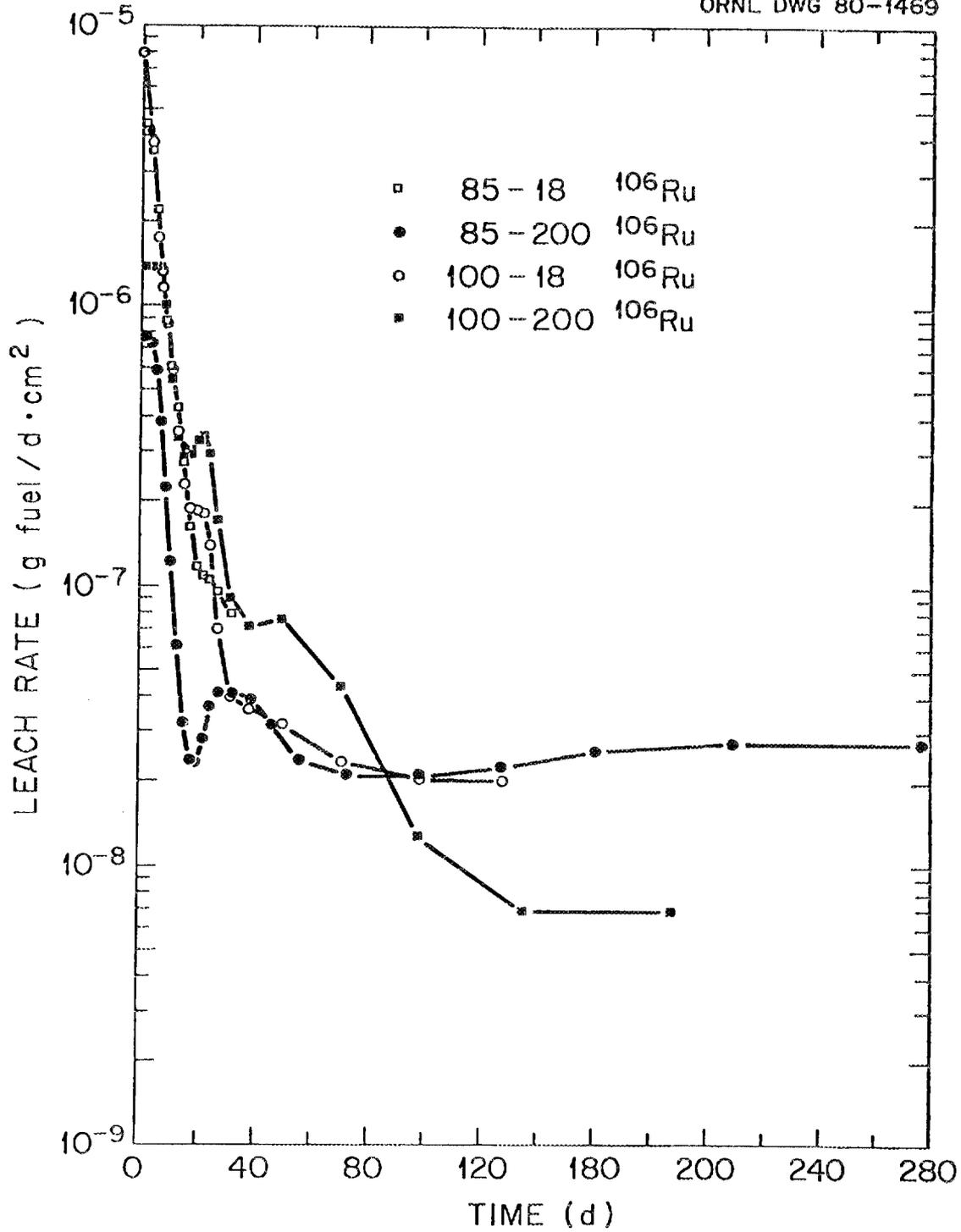


Fig. 11. Leach rates for ¹⁰⁶Ru.

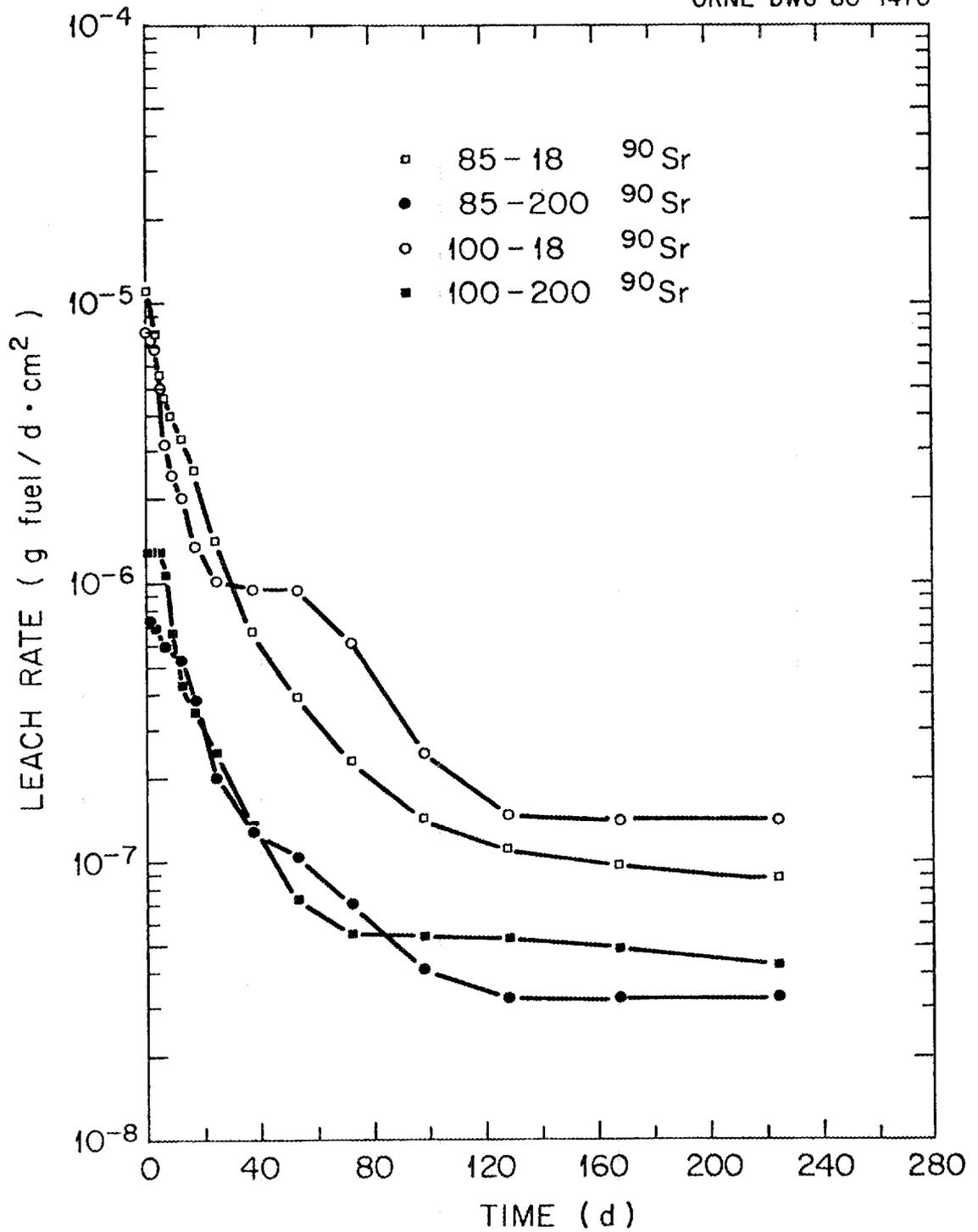


Fig. 12. Leach rates for ⁹⁰Sr.

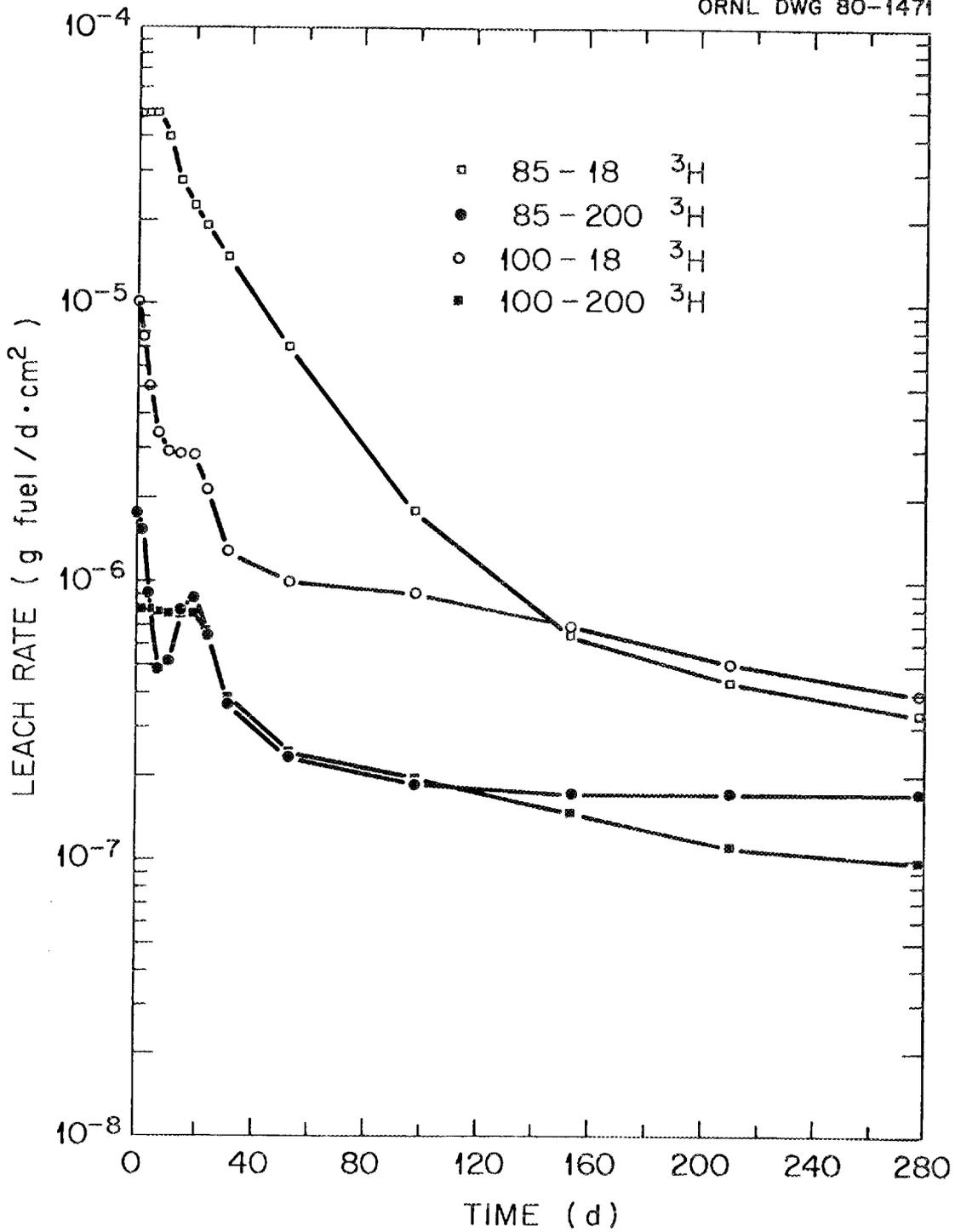


Fig. 13. Leach rates for ³H.

fuel fragments release tritium at a faster rate than do the small fragments.

5.2 Cumulative Leach Fraction

An integration of leach rate over time gives the total fraction of the particular substance that was released from the fuel. For these experiments, the leach fraction was determined by two methods. In trial 100-50, in which the leachant was replenished rather than replaced, the cumulative fraction was being measured directly. The leach rate was the quantity measured in trials 85-18, 85-100, 100-18, and 100-200; some calculations were required to obtain the fractional release.

For trial 100-50, the cumulative leach fraction was calculated by summing the amount of the solute contained in the leaching vessel with the amounts of solute removed during sampling. These results were not smoothed because of the small number of data points.

The leach rate data for trials 85-18, 85-200, 100-18, and 100-200 were smoothed and numerically integrated over time. The integration was performed by assuming that the logarithm of the rate varied linearly from one data point to the next. Thus, for the interval of time t_{i-1} to time t_i , the rate is described by

$$\ln(R_i) = a_i t + b_i , \quad (3)$$

where

$$a_i = [\ln(R_i) - \ln(R_{i-1})] / (t_i - t_{i-1}) , \quad (4)$$

and

$$b_i = [t_i \ln(R_{i-1}) - t_{i-1} \ln(R_i)] / (t_i - t_{i-1}) . \quad (5)$$

The values for a_i and b_i are regarded as constants over the time interval. For this analysis the leach rate is in terms of fraction per day, or

$$R_i = x_i / x_0 (t_i - t_{i-1}) \quad (6)$$

in the notation of Eq. (2). It is then an easy matter to calculate the fractional release over that time interval by using

$$F_i = \int_{t_{i-1}}^{t_i} \exp(\alpha_i t + b_i) dt \quad (7)$$

and over the course of the experiment by using

$$F = \sum_{i=1}^n F_i . \quad (8)$$

This procedure was applied to the smoothed data unless noted otherwise.

Figure 14 shows the results for uranium. The fractional release of uranium into the leaching solution is less than 1E-3 for all five trials. The larger particles have a significantly smaller fractional release, and higher temperature seems to inhibit the release of uranium.

Figure 15 shows the release of gross alpha activity, or plutonium. The cumulative release is about a factor of 5 smaller than that for uranium. The curves for the larger particles show a definite leveling off after 20 d, whereas the smaller particles continue to release activity. The explanation for this behavior is not clear.

As was the case with the leach rates, fractional release curves for cerium and europium would be expected to follow those for uranium. Figure 16 shows the curves for ^{144}Ce . The results for trials 100-18 and 100-200 are very similar to those for uranium. However, the results for 85-18 and 85-200 show a significantly smaller release fraction. The curves for ^{154}Eu , shown in Fig. 17, are very similar to and tend to confirm the uranium results.

It would be expected that semivolatile fission products would have larger fractional releases than was observed for uranium and the rare earths. This is indeed the case, as is shown for ^{134}Cs and ^{137}Cs in Figs. 18 and 19, respectively. About 4E-4 of the uranium was released, and $\sim 3\text{E}-3$ of the cesium was leached from the fuel. Slightly more cesium is released at the higher temperature; the influence of particle size is unclear.

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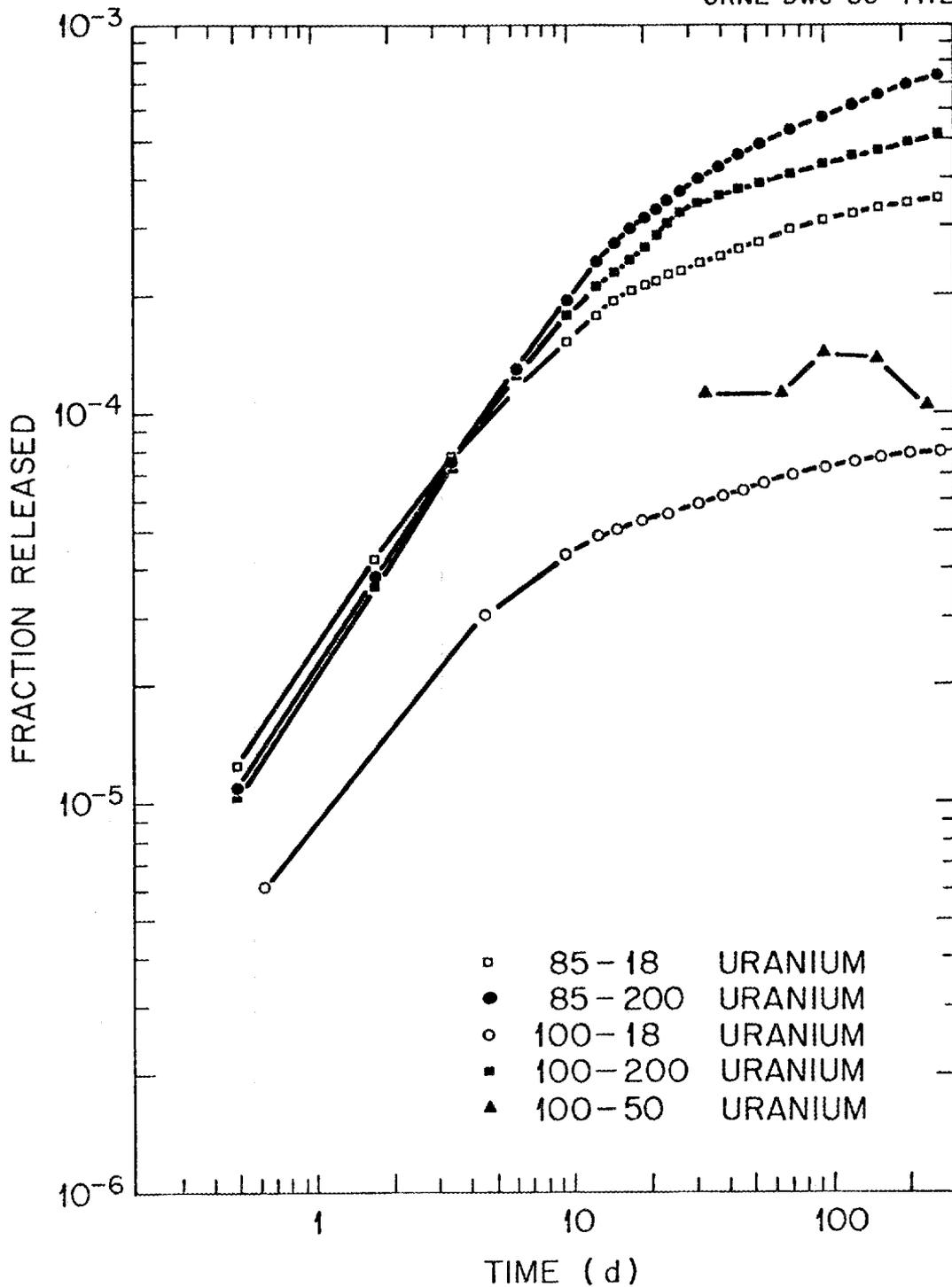


Fig. 14. Fractional releases for uranium.

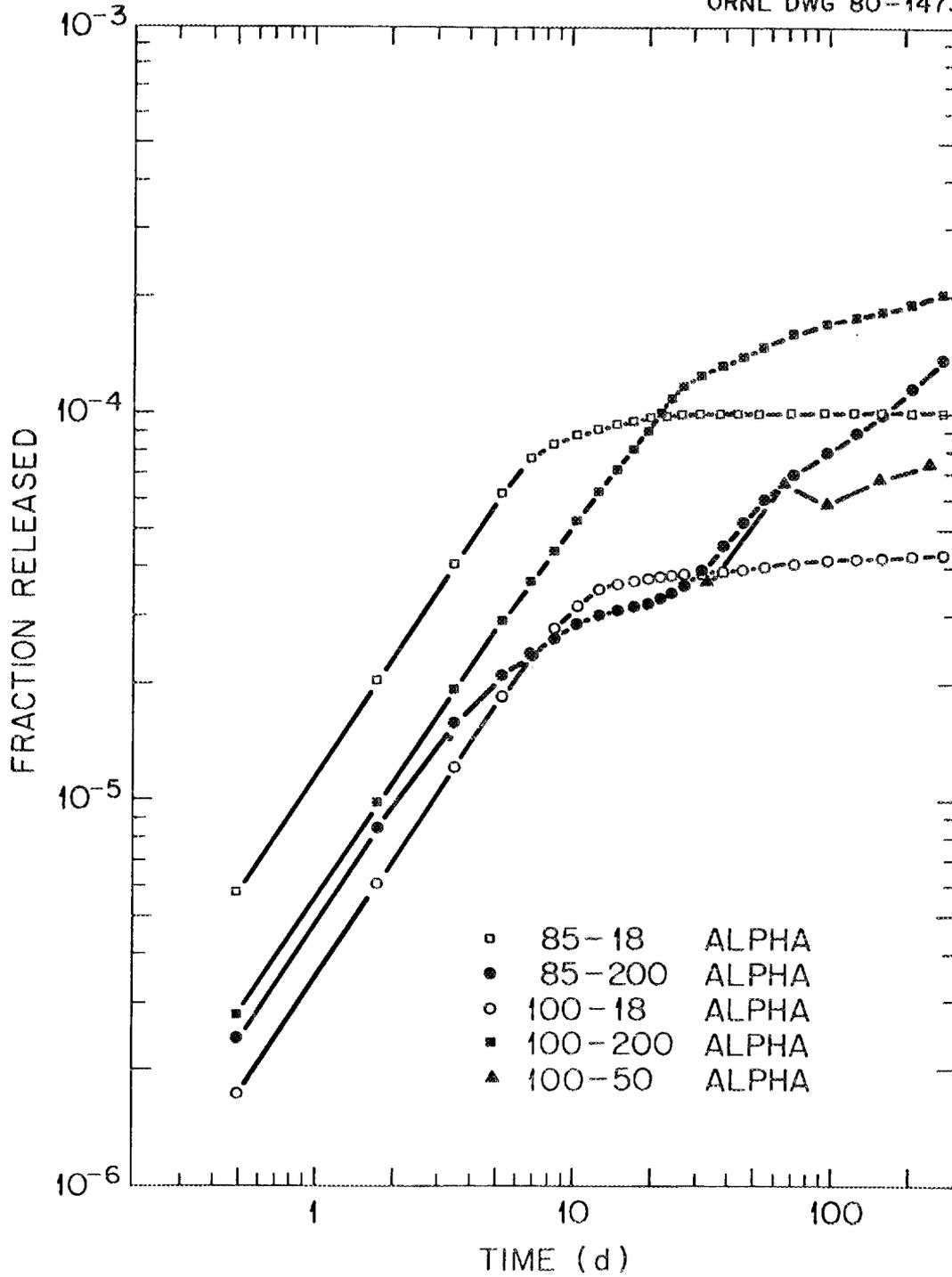


Fig. 15. Fractional releases for gross alpha activity.

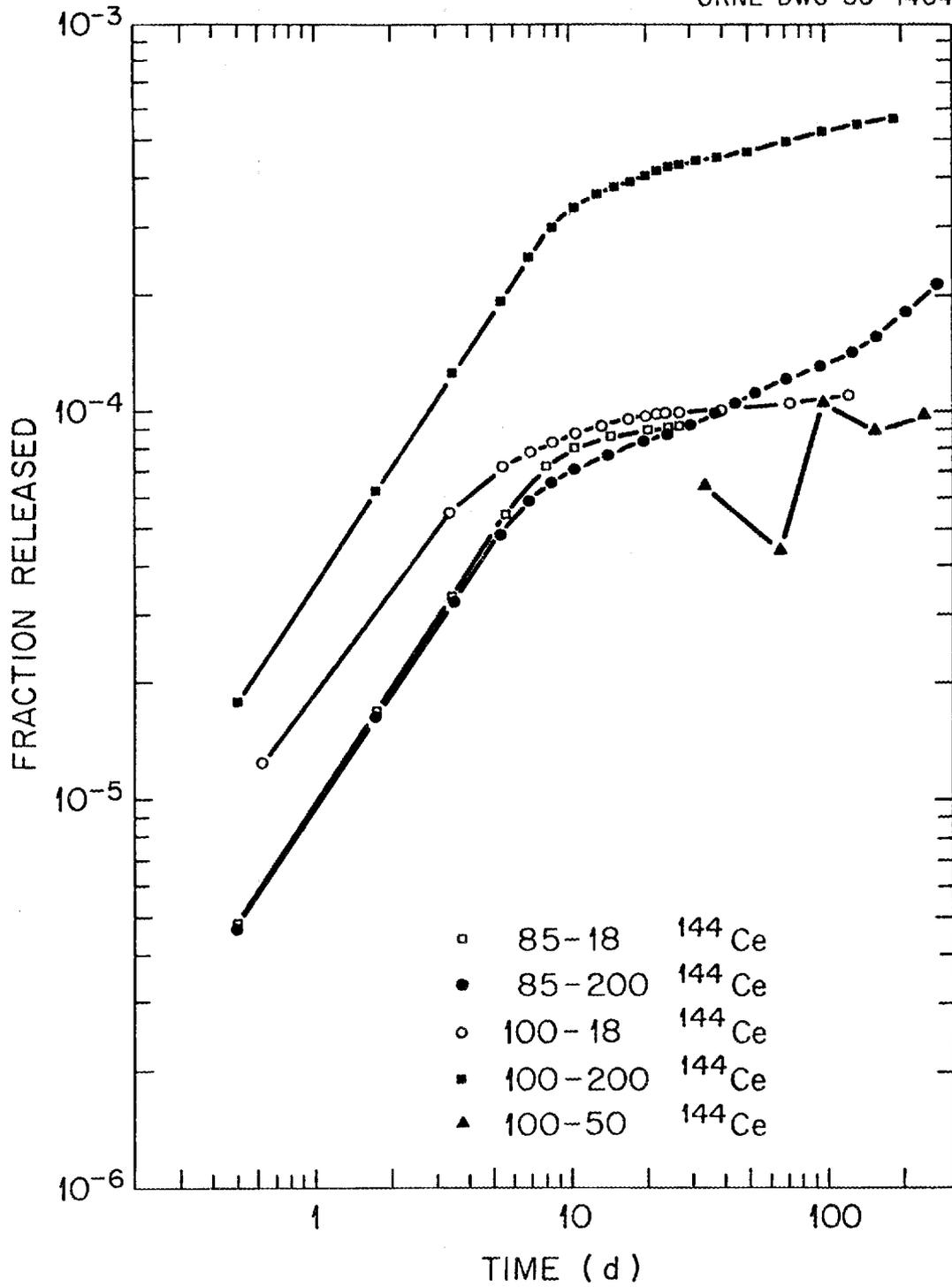


Fig. 16. Fractional releases for ¹⁴⁴Ce.

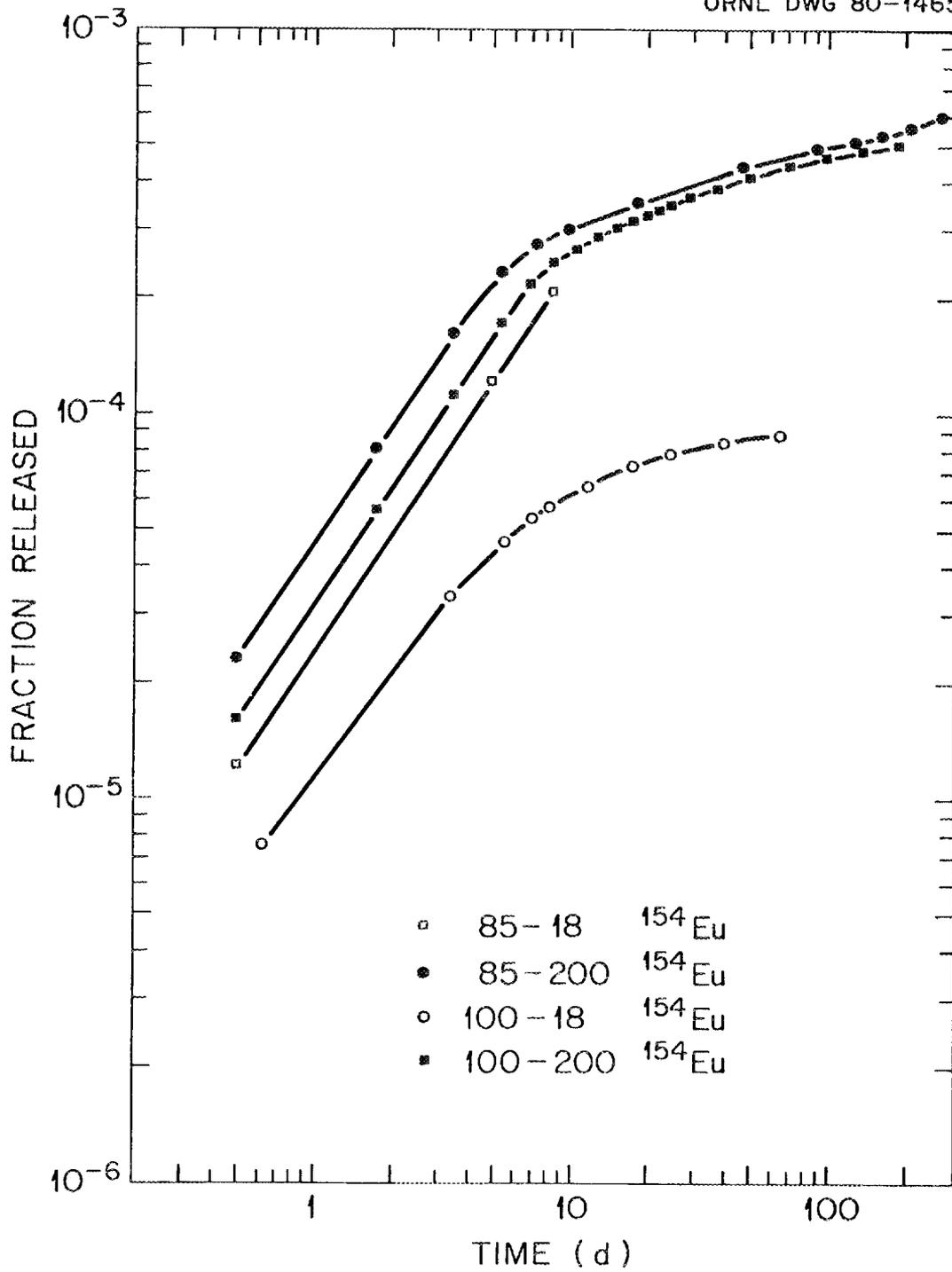


Fig. 17. Fractional releases for ¹⁵⁴Eu.

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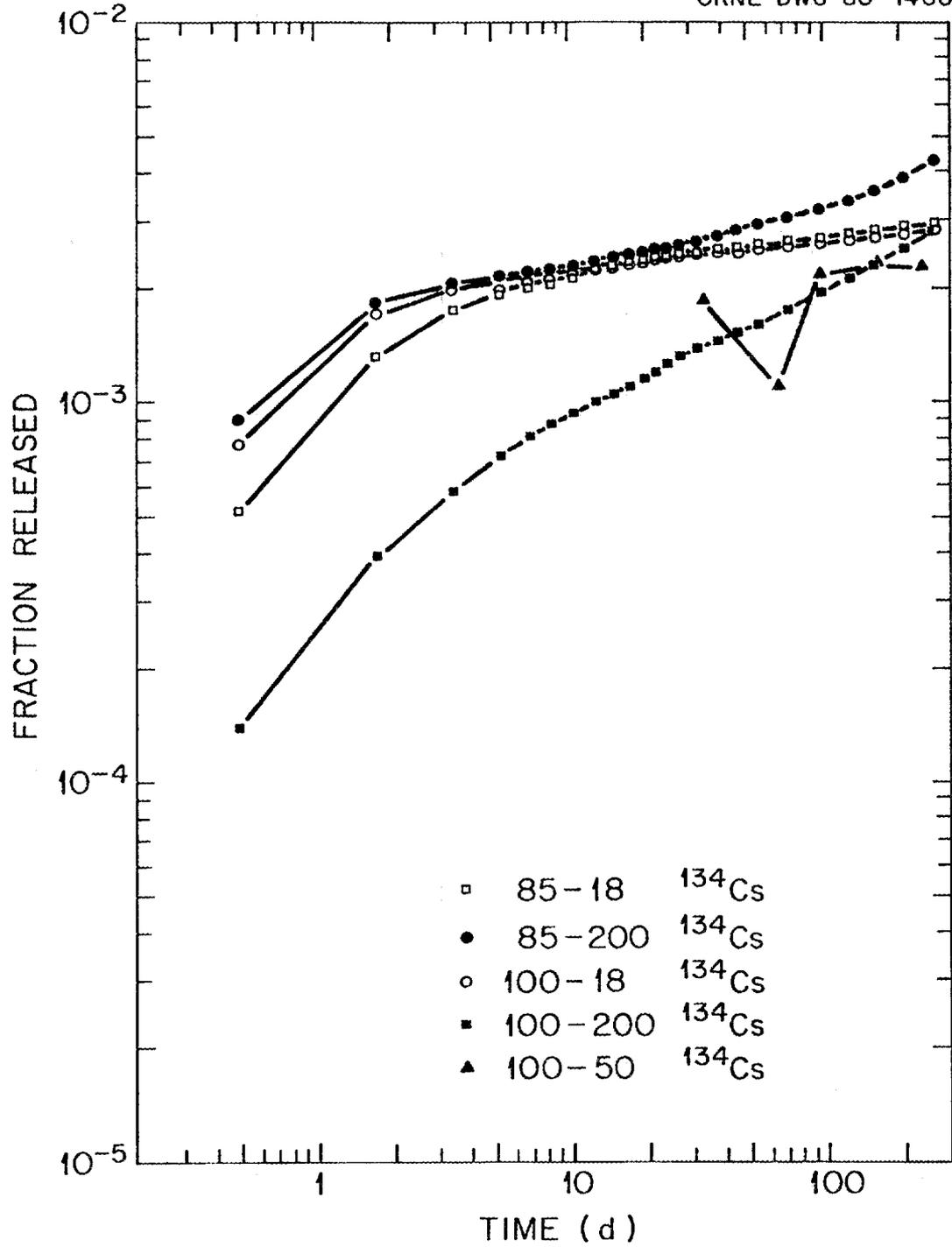


Fig. 18. Fractional releases for ^{134}Cs .

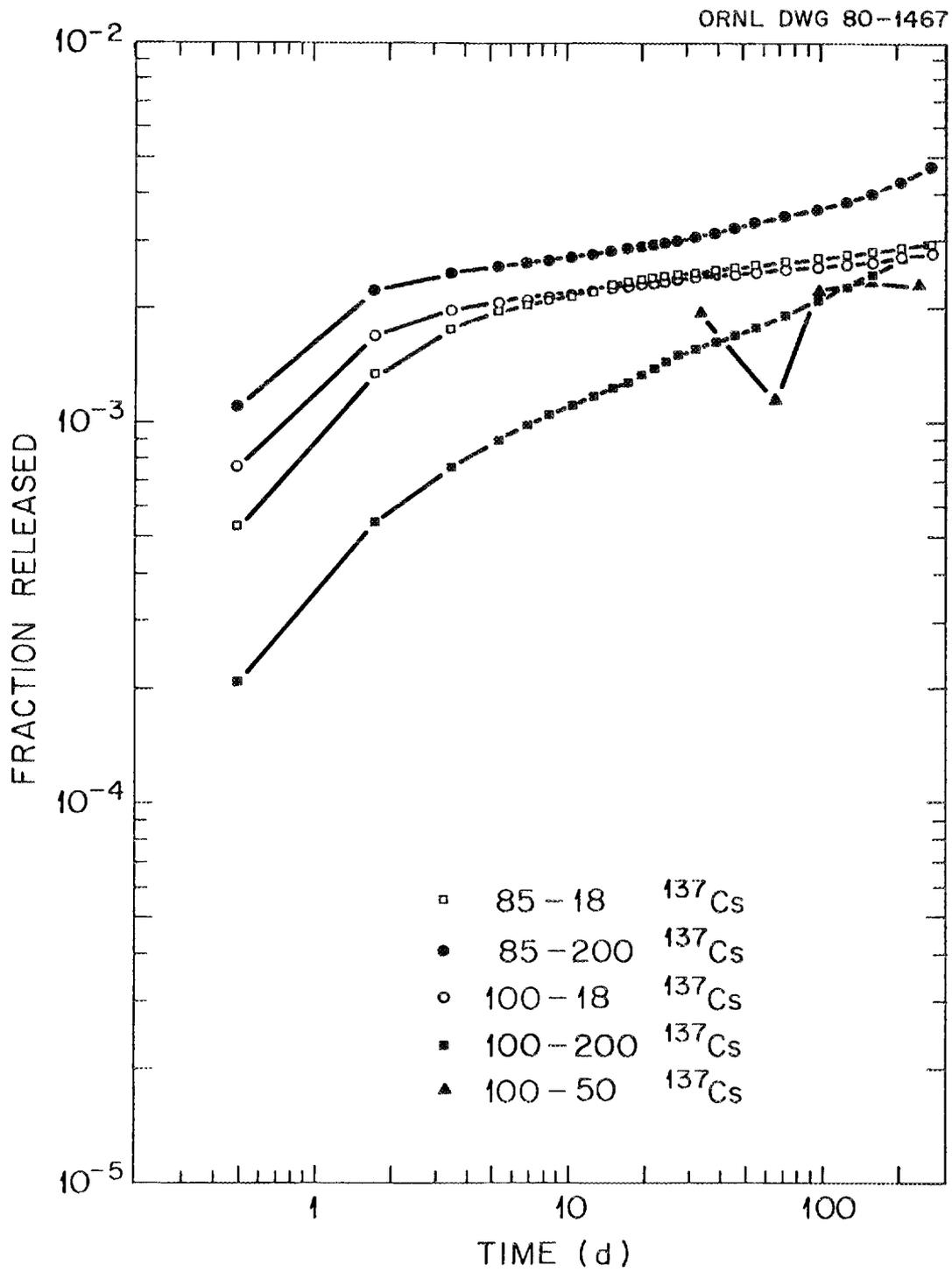


Fig. 19. Fractional releases for ^{137}Cs .

It is suspected that iodine occurs in the fuel as CsI; thus, the amount of iodine released should be similar to the amount of cesium. Figure 20 shows the fraction of ^{129}I released. The rate data were not smoothed prior to the integration procedure for this plot because of the small number of data points. The fractional release is $\sim 6\text{E-}2$, or 20 times higher than that for cesium. Again, this is due to the larger inventory of cesium in the fuel ($\sim 15 \mu\text{mol}$ of cesium per g of fuel vs $\sim 0.9 \mu\text{mol}$ of iodine per g of fuel). When the two substances are compared in terms of micromoles released, as in Fig. 21, the leaching of CsI cannot be dismissed.

The results for antimony (see Fig. 22) indicate a total release of $\sim 6\text{E-}3$, which is slightly higher than the fractional release of cesium. The temperature does not have a consistent influence on the results; however, the smaller particles apparently release a larger fraction of their inventory to the leach solution than do the larger particles.

Ruthenium is released from the fuel to about the same extent as uranium. Figure 23 shows that $\sim 4\text{E-}4$ of the ^{106}Ru initially present in the fuel is released to the leachant within the first year. The release fraction appears to be enhanced by elevated temperatures and by small particle sizes.

Figure 24 gives the results for strontium. About $8\text{E-}4$ of the inventory was released from the fuel during these experiments. Although the influence of temperature is not very definitive, particle size appeared to be important since the small particles released slightly more strontium than did the larger particles.

Figure 25 shows the curves for tritium. The cumulative release is $\sim 3\text{E-}3$ after 1 year. No conclusive effect of temperature or particle size is seen.

The fact that the data for trial 100-50 are unusually very near the curves for the other four trials is encouraging. This tends to validate both the numeric integration scheme and the results of the analyses. It also indicates that the ions previously leached from the fuel do not significantly retard or enhance further leaching of the fuel. The single

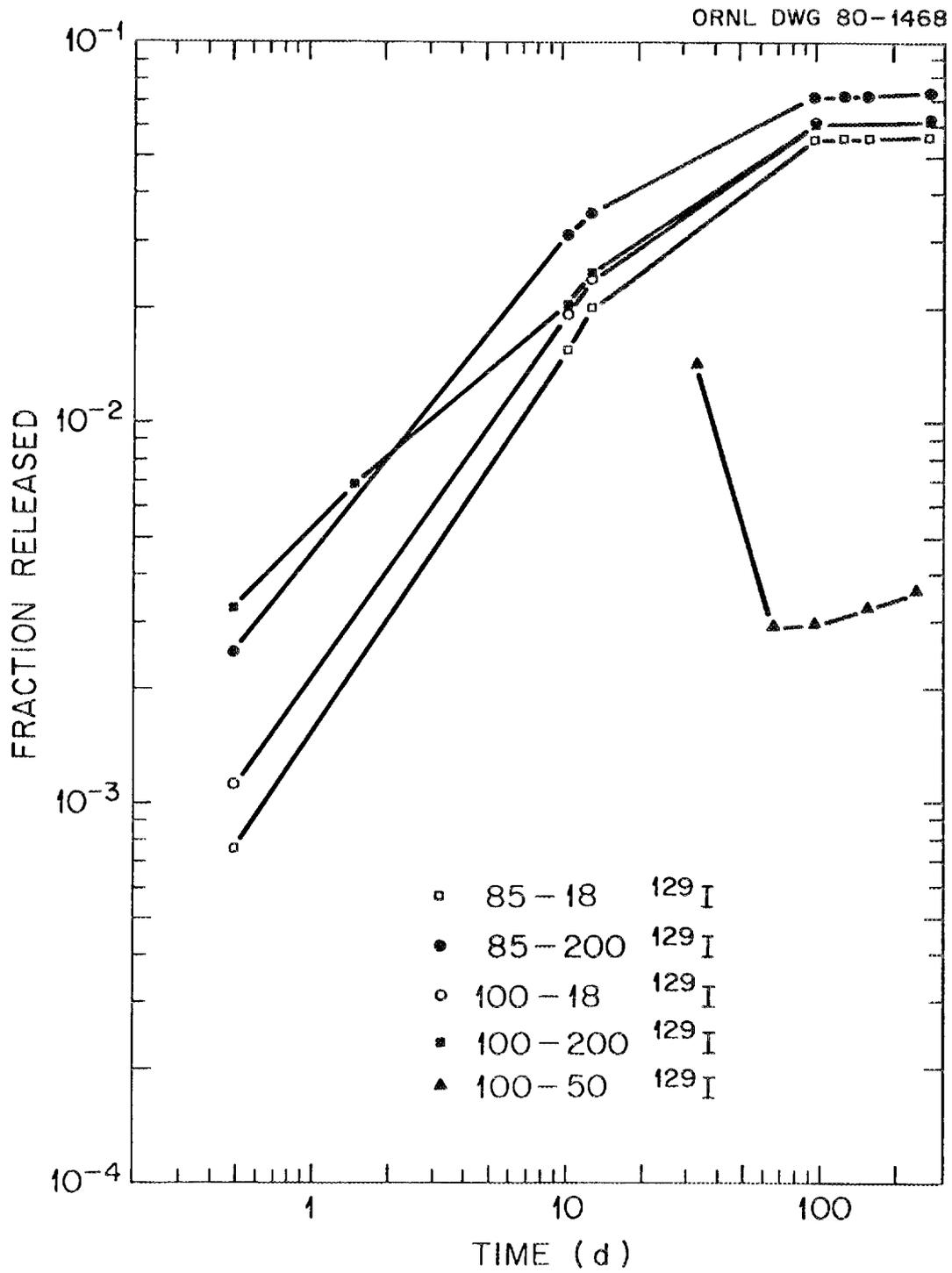


Fig. 20. Fractional releases for ^{129}I .

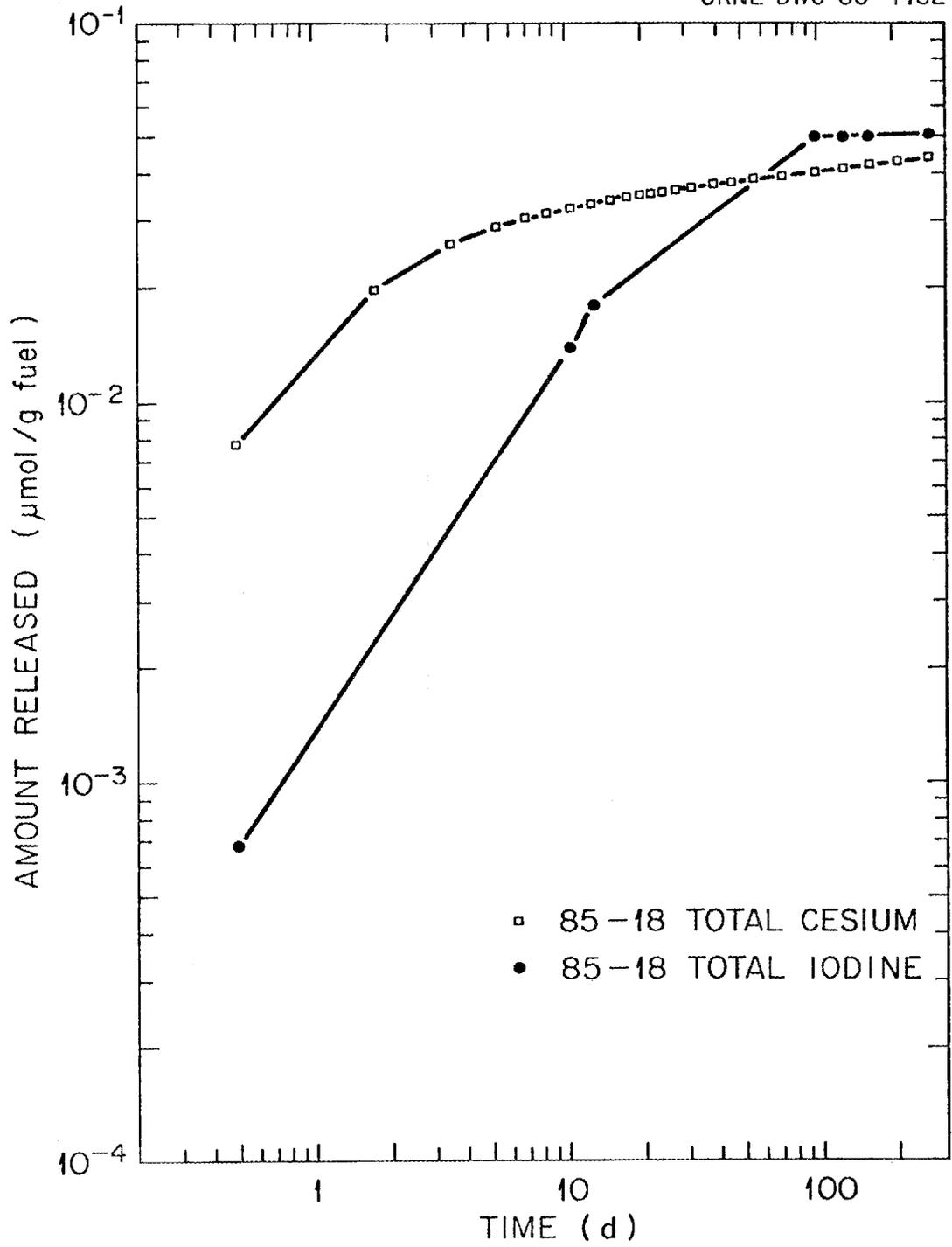


Fig. 21. Comparison of amounts of total cesium and total iodine released.

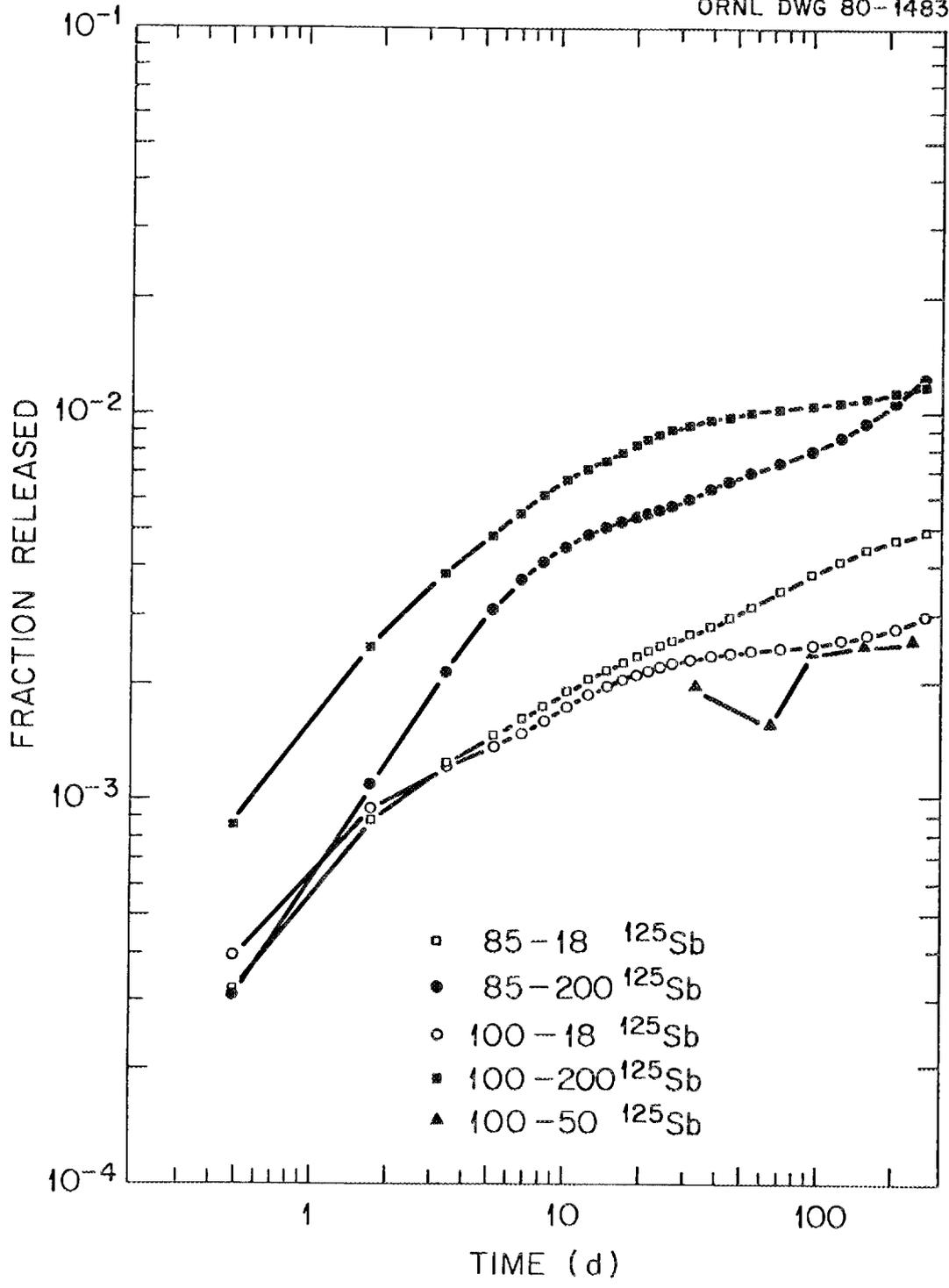


Fig. 22. Fractional releases for ^{125}Sb .

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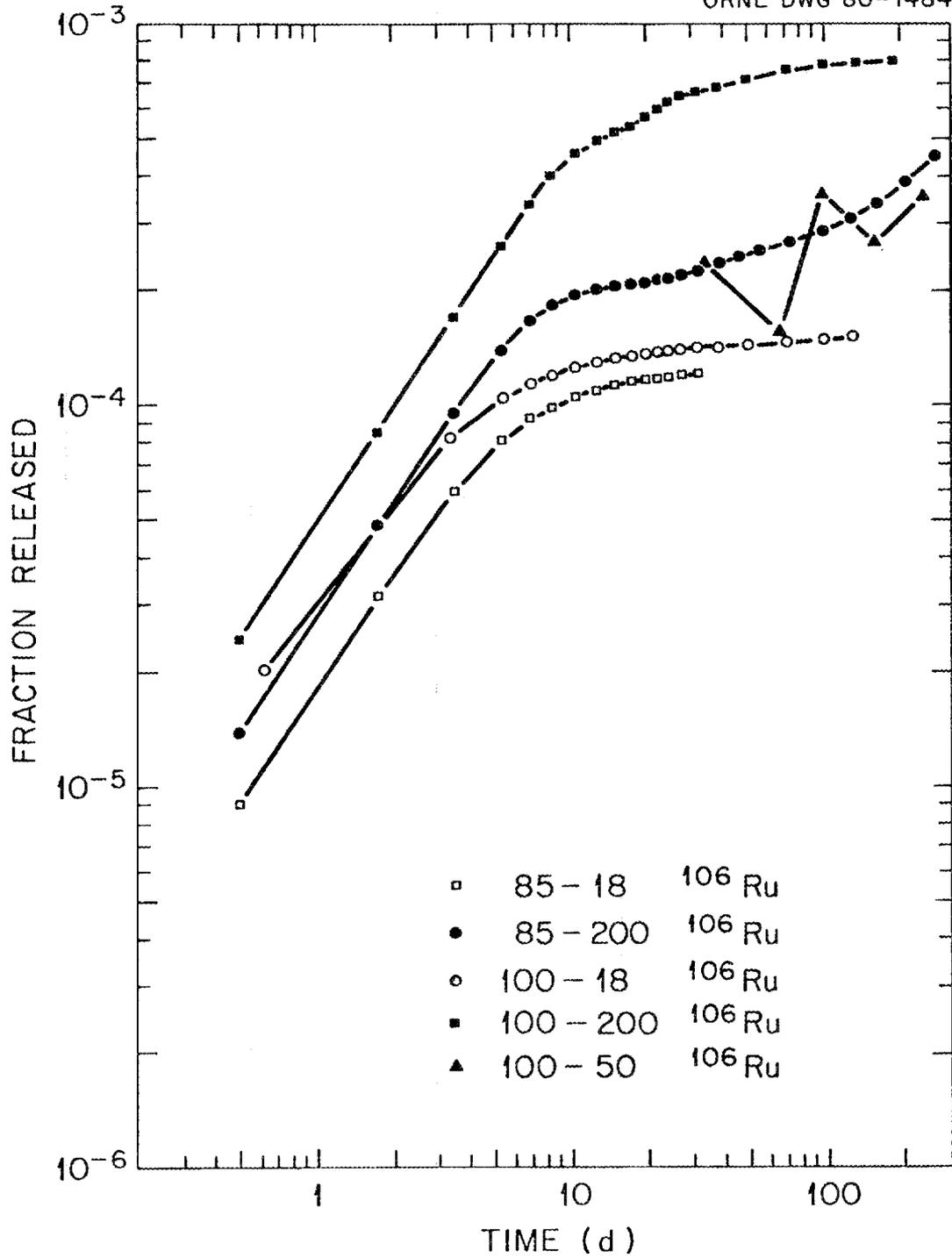


Fig. 23. Fractional releases for ^{106}Ru .

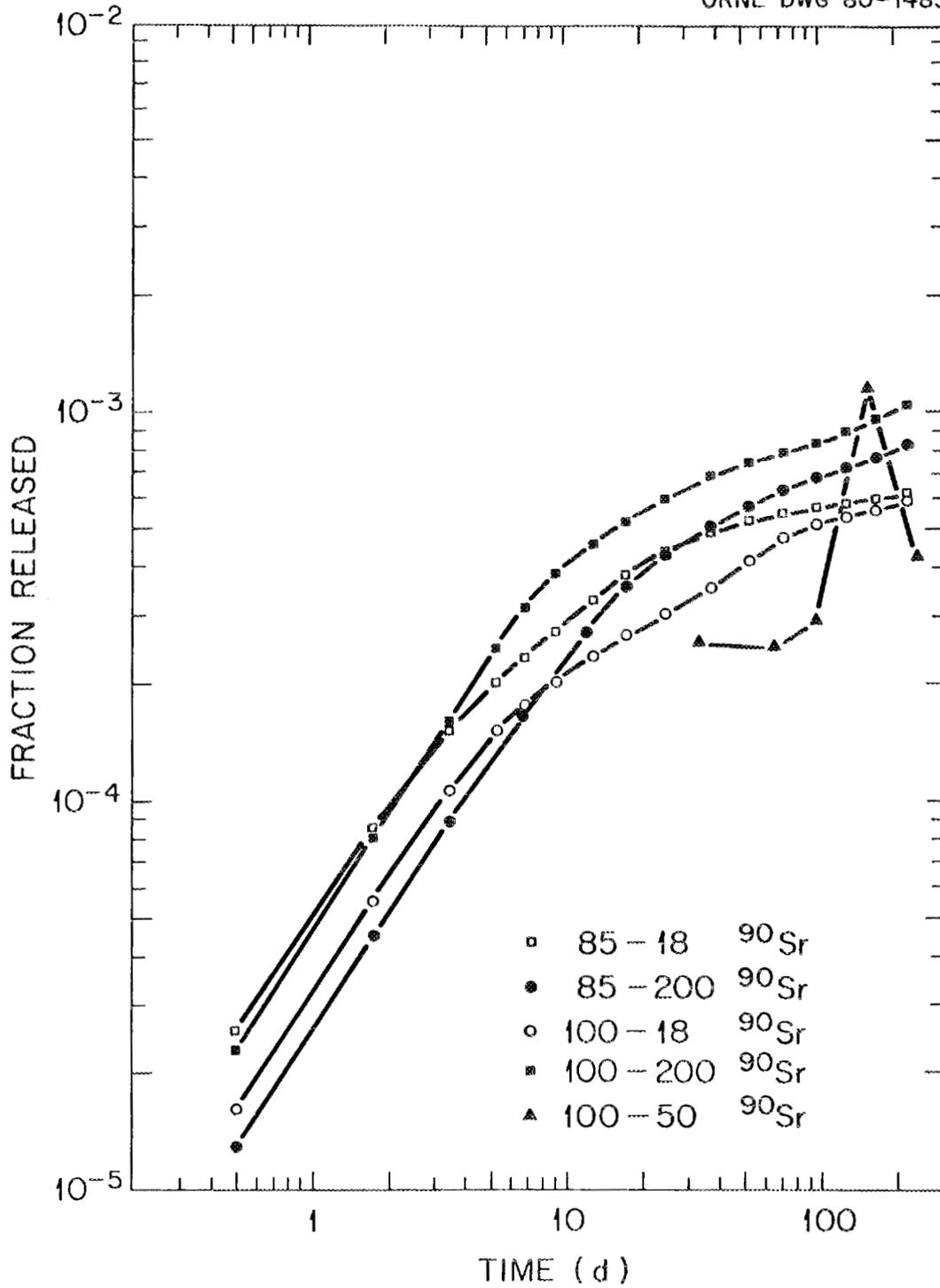


Fig. 24. Fractional releases for ⁹⁰Sr.

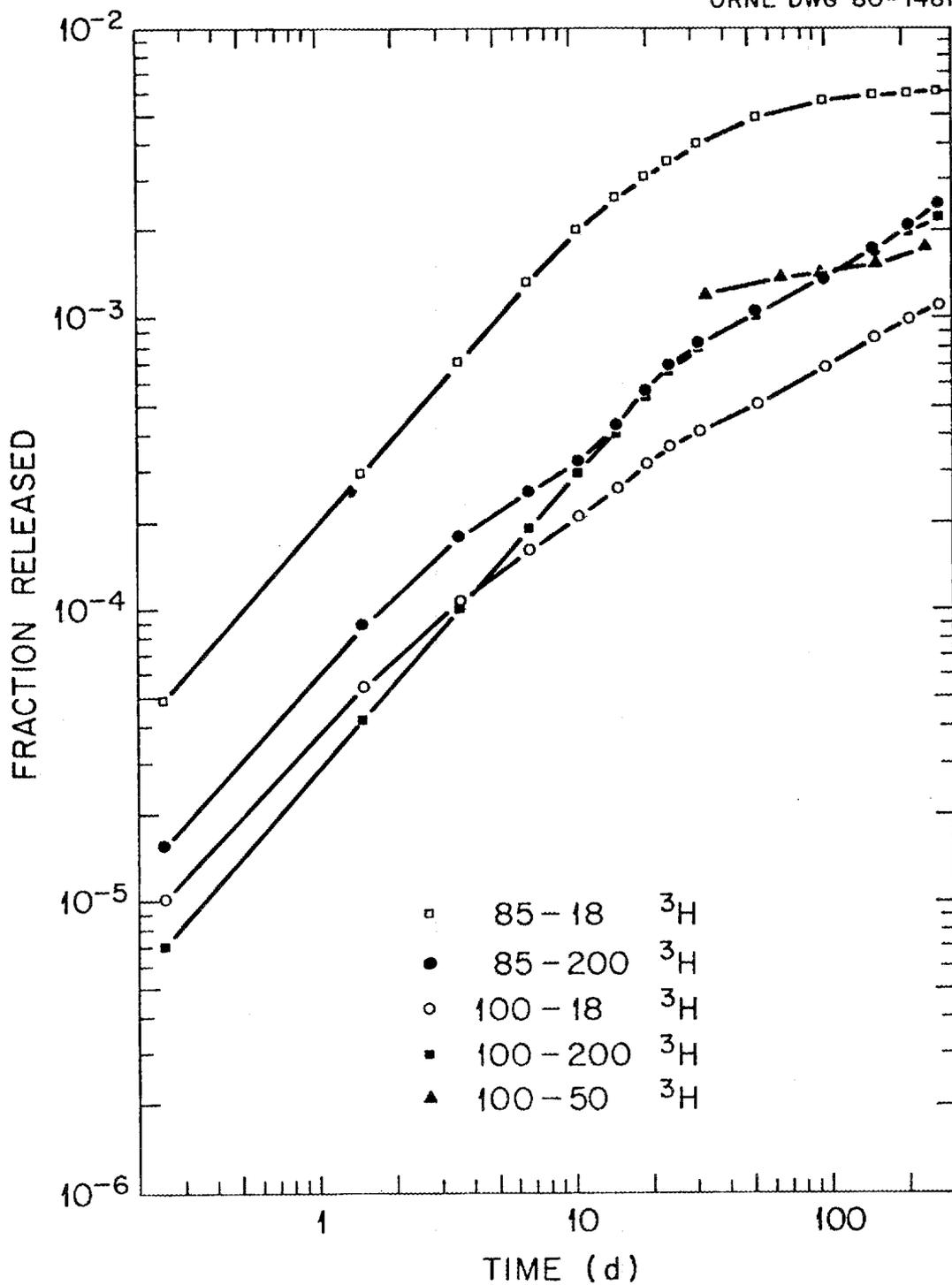


Fig. 25. Fractional releases for ³H.

exception is the fraction of ^{129}I released in trial 100-50, which was only one-tenth of that released in the other trials. The reason for this difference is not clear.

6. DISCUSSION OF RESULTS

The results of these experiments should be helpful in planning for the cleanup of a damaged nuclear facility. The tests measured the leach rates and fractional releases for important fission products, and also indicated the influence of temperature and particle size. The values obtained are similar to those of other investigators. However, the limitations of these experiments must be considered before the results are applied to a real situation.

The relative rate of leaching, as measured at the end of these tests, is $\text{Sb} > \text{I} > {}^3\text{H} > \text{Cs} > \text{Sr} > \text{Ru,Ce,Eu,U} > \text{Pu}$. The long-term rates are bracketed by $\sim 5\text{E-}7$ g fuel/d $\cdot\text{cm}^2$ for antimony and $\sim 2\text{E-}9$ g fuel/d $\cdot\text{cm}^2$ for plutonium.

The ranking by fractional release can be summarized as follows: $\text{I} > \text{Sb} > {}^3\text{H,Cs} > \text{Sr} > \text{Ru,Ce,Eu,U} > \text{Pu}$, after 250 d of leaching. The releases for iodine and plutonium are $\sim 6\text{E-}2$ and $\sim 1\text{E-}4$, respectively. These releases can be used to estimate the reactor-water concentration by multiplying the fractional release by an estimation of the fuel inventory and an estimation of the amount of fuel open to leaching, and then dividing the product by the volume of water. To project the release fraction curves (Figs. 14-25) to future times, the long-term fractional releases were fit to the form of Eq. (1) to obtain a value for m . This value is simply the slope of the long-term line in Figs. 14-25. The break between "long term" and "short term" was made by identifying the time at which the fractional-release curves change slope. This time is usually within the first month of leaching. In several cases, this break was clear and the time was easy to determine; in other cases, the break was chosen more subjectively. In one case no break was seen because of a lack of long-term data; consequently, no value is reported. The values for the exponent m in Eq. (1) are given in Table 3. The results show that the

Table 3. Value for m in $F = Bt^m$

Substance	Trial				Av
	85-18	85-200	100-18	100-200	
Uranium	0.21	0.34	0.17	0.19	0.23
Gross alpha	0.01	0.57	0.07	0.22	0.22
^3H	0.13	0.59	0.47	0.49	0.42
^{90}Sr	0.12	0.29	0.37	0.28	0.27
^{106}Ru	0.12	0.23	0.07	0.14	0.14
^{125}Sb	0.31	0.28	0.11	0.10	0.20
^{129}I	0.02	0.03	0.02	0.03	0.02
^{134}Cs	0.10	0.17	0.07	0.33	0.17
^{137}Cs	0.09	0.16	0.07	0.30	0.15
^{144}Ce	0.13	0.32	0.08	0.17	0.17
^{154}Eu		0.20	0.17	0.23	0.20
Av	0.12	0.29	0.15	0.22	

exponent is larger for the smaller particles and that temperature has no apparent effect. The results also show that some substances (notably, tritium) have a higher exponent than the others. This does not mean that tritium had a faster leach rate at the termination of these experiments, but rather that tritium will probably be the first substance to completely leave the fuel. Projected fractional releases are given in Table 4. These estimates were made by extending the curves in Figs. 14-25 with a straight line [as defined by Eq. (1)] and finding the minimum and maximum values produced. The minimum values were always given by the 18-mesh fuel fragments; the maximum estimate was generally given by the 200-mesh fragments. The only exception is that both the minimum and maximum values for tritium were given by the 18-mesh fragments. These values can be used to estimate reactor-water concentrations at future times.

These experiments were designed to determine the influence of temperature and particle size on leach rate and released fraction. While the size of the fuel fragment was found to have a definite effect, the temperature data were inconclusive.

Table 4. Estimated percentage of fuel inventory leached from the fuel over time

Substance	Time (y)			
	1	2	3	4
Uranium	0.009-0.087	0.010-0.11	0.011-0.13	0.011-0.14
Gross alpha ^a	0.004-0.022	0.005-0.026	0.005-0.030	0.005-0.036
³ H	0.13-0.64	0.18-0.70	0.21-0.74	0.24-0.76
⁹⁰ Sr	0.066-0.12	0.072-0.15	0.076-0.16	0.079-0.18
¹⁰⁶ Ru	0.016-0.093	0.017-0.10	0.018-0.11	0.018-0.11
¹²⁵ Sb	0.30-1.2	0.32-1.5	0.33-1.6	0.34-1.8
¹²⁹ I	5.6-7.4	5.7-7.5	5.7-7.6	5.8-7.6
¹³⁴ Cs	0.29-0.41	0.30-0.46	0.31-0.49	0.32-0.52
¹³⁷ Cs	0.28-0.46	0.30-0.51	0.30-0.55	0.31-0.57
¹⁴⁴ Ce	0.012-0.066	0.013-0.074	0.013-0.079	0.014-0.083
¹⁵⁴ Eu	0.012-0.063	0.014-0.073	0.015-0.080	0.016-0.086

^aPlutonium.

The apparent influence of temperature on the various substances was noted in Sect. 5. The only consistent effects found were an increase in the strontium leach rate and a decrease in the uranium leach rate as the temperature was increased from 85 to 100°C. The data obtained at the other leach rates did not show any definitive trend. There were enough data on eight of the substances studied to make a determination of the effect of temperature. If determined solely by chance, one would expect one-fourth of the results to show an increased leach rate with temperature and one-fourth to show a decreased rate. This was the situation observed in our tests; thus, because neither of the apparent effects was clearly decisive, we conclude that the temperature trends noted in Sect. 5 were only fortuitous results.

The influence of particle size can be seen more clearly. Of the seven substances for which there were sufficient data, six showed an increased leach rate with increased fuel-fragment size. Thus, a definite effect was observed, and only a fraction of the effect can be ascribed to the inaccuracy of the surface area measurement. This effect is also reflected by the values for the exponent m in Table 2 and in the fractional releases. Although the larger particles had a higher leach rate (in units of g fuel/d·cm²), they had a smaller fractional release (in units of fraction of substance inventory) by a factor of ≈ 3 . The apparent inconsistency between the higher leach rate resulting in a smaller fractional release is simply due to the units of the rate and the disparity in the surface area per gram of fuel for the two particle sizes.

The results of these tests compare favorably with those of previously published work. The relative rate of leaching is Cs > Sb > Sr > Pu according to Katayama,² Cs > Sr > Ce > Pu according to Strathdee et al.,⁴ and Sb > I > ³H > Cs > Sr > Ru,Ce,Eu,U > Pu according to our tests. The only change in order is between cesium and antimony. The values for the leaching rates are lower than those reported by Katayama by about a factor of 5. This may be because he reports the rates at 20 weeks rather than 40 weeks. These results may also reflect the use of a borate leach solution. The values for the exponent m correspond well with the range (0.06-0.35) found by Katayama² for distilled water. For the individual isotopes, Katayama found 0.07 to 0.35 for ⁹⁰Sr and 0.06 to 0.32 for ¹³⁷Cs. These values compare favorably with the range found in the study reported here. (The agreement is not too surprising when we consider the large range involved.)

There were several shortfalls in our experiments that must be considered in the interpretation of the results. The controls on the leaching conditions left open some variables (such as the oxygen contents of the solutions) that may have an important influence on the outcome. The analyses for some of the substances studied had significant levels of uncertainty; consequently, the results cannot be used as exact

measures of the quantities involved. In addition, the surface area measurement was not very precise, and the accident conditions prior to a cladding failure were not simulated.

As stated in Sect. 2, many investigators carefully control the reducing or oxidizing potential of their leaching solution. They find that the oxidizing potential has an effect on leach rates in some cases. The results of the work of Norris⁵ and Bryant⁶ demonstrate that leaching is slower in a reducing environment. Reactor water is normally kept reducing, or oxygen-free, to inhibit corrosion of the metal surfaces. We made no special effort to exclude oxygen from the leaching solutions; thus, leaching in a reactor vessel should proceed at the same speed as, or slower than, that in our experiments.

The concentrations of some of the substances were near the minimum analytical detection level; therefore, the results contained only one significant digit in some cases. This was true for uranium, cerium, europium, and (to a lesser extent) ruthenium. The lack of significant digits prohibits literal interpretation of the results. However, because the concentration range being studied is so large, even an error band of 20 or 30% is minor when plotted on a logarithmic scale. Although iodine levels were in the range of analytical capability, about one-half of the estimated initial inventory was unaccounted for at the conclusion of the experiment. Prior measurements and calculations determined that there was ~ 90 μg of ^{129}I per gram of fuel. When the tests were completed and four fuel samples were dissolved, ~ 44 $\mu\text{g/g}$ fuel was found, and ~ 5 $\mu\text{g/g}$ fuel was present in the leaching solutions. The fate of the remainder is unknown.

As stated previously, the surface areas of the samples were not measured very accurately. This deficiency has two significant effects on the interpretation of the results:

1. Other investigators have expressed leach rate results on a "per surface area" basis, as we have. Because none of them has measured surface area exactly, the values cannot be compared among investigators with any degree of reliability.

2. The inexact measurement of surface area presents a problem in comparing one particle size with another. Our results can be trusted in identifying large effects (factors of 10) of particle size because the surface area measurements are consistent with each other; however, the results cannot be used to identify small effects (factors of 1.5) because the measurements are not that precise.

We did not consider fission-product release during the initial rupture of the rod or any effects of cladding oxidation. Lorenz et al. found that the burst release of cesium and iodine would be <0.1% of the total inventory,¹ which would be a small addition to the total amount released in our experiments.

The results presented here will provide useful information concerning the fraction of the fission-product inventory that will be found in the water surrounding a damaged reactor core prior to cleanup operations. Leach rates and fractional releases will be important in choosing and in scaling the process used for the cleanup. Although the agreement between our results and those of other investigators is good and tends to confirm our findings, it is still important to recognize the limitations in the experiments reported here.

7. CONCLUSIONS

The following conclusions can be drawn from the results obtained in this study:

1. The relative speed of leaching the constituents of spent fuel after 250 d has been determined to be: $Sb > I > {}^3H > Sr > Ru, Ce, Eu, U > Pu$; the range is from $\sim 5E-7$ g fuel/d·cm² for ¹²⁵Sb to $\sim 2E-9$ g fuel/d·cm² for plutonium.
2. The relative releases after 250 d, as a fraction of total inventory, can be summarized as: $I > Sb > {}^3H, Cs > Sr > Ru, Ce, U > Pu$; the range is from $\sim 6E-2$ for iodine to $\sim 1E-4$ for plutonium.

3. The value for the exponent m in Eq. (1) varies from 0.01 to 0.59, depending on the substance studied and the leaching conditions.
4. Assuming the validity of Eq. (1), the fractional release of the various substances can be projected for future times.
5. No significant temperature effect was found for the leach rates.
6. The leach rates (in units of $\text{g fuel/d}\cdot\text{cm}^2$) of the substances studied were higher for the larger particle sizes.
7. The fractional releases of the substances studied were smaller for the larger particle sizes by a factor of ~ 3 .

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