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BASIC RESEARCH FOR EVALUATING NUCLEAR WASTE FORM PERFORMANCE

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Abstract

To serve as an introduction to the basic research needs involved with waste form performance, background information is presented on nuclear waste types and relative toxicities, and scenarios for radionuclide release. Some results from present studies on nuclear waste leaching experiments are discussed to show where added research is deemed necessary. To understand the leaching mechanisms of importance, techniques for determining waste form surface structural and compositional changes and radionuclide chemical species and valence states in solution must be put into practice.

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Introduction

To provide for analysis of the consequences of nuclear waste isolation we must develop a data base for understanding the major processes involved in waste form alteration, interactions with engineered barriers, and radionuclide transport out of the waste package system. Because of the complexity of the multiple barrier interaction system however, current testing programs to date have been concentrating on binary subsets of this system, such as waste form - solution leaching experiments. Although we are now starting tests that are aimed at studying the waste package system, there remains a good deal of research work to be done to better understand the processes involved in leaching, waste form alteration, and radionuclide migration.

An insight into the areas of basic research needed may be gained by looking at the present status of waste form and leaching data base. A brief discussion of this data is given in the text of the paper. Using this information we find that the major areas of needed research center around solid surface structure and detailed radionuclide solution analysis.

Discussion

One of the major areas of research related to nuclear energy today is that of the consequences of nuclear waste isolation in geologic media. The purpose of this presentation is to provide an overview of waste form performance studies, including needed basic research studies. The major areas I will discuss are:

- introduction to the general problem,
- waste-rock interaction in a repository,
- current status of experimental programs on waste form performance, and
- basic research needed to support repository licensing.

What we are trying to accomplish in research on waste form performance is to provide input to release consequence analyses such that credible safety estimates can be made for geologic repositories.

To provide an analysis of the consequence of nuclear waste insolation it is necessary that we develop a data base for understanding the major processes involved in waste form alteration, radionuclide release and subsequent migration to the biosphere. While this is obviously a challenging objective, I believe that it can be accomplished and that it will be a central issue in the repository licensing process. The mathematical models used for safety assessment need to be constructed using experimental data based on appropriate "basic science" input, and ultimately verified by testing and/or studies on related natural phenomenon.

To give an indication of the emphasis on nuclear waste management the expenditures in this area are listed in Table 1.(1)

TABLE 1. AEC, ERDA, and DOE Budget Expenditures for Nuclear Waste Management

Fiscal Year	Budget (millions $)[1]
1967 and prior years	206
1968	21
1969	26
1970	28
1971	32
1972	46
1973	48
1974	61
1975	94
1976	158
1977	230
1978 estimated	374
1979 estimated	449

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[1] All figures are rounded. Includes facility construction as well as operating dollars.

The classes of nuclear wastes and their primary generation sources are listed in Table 2.(2)

TABLE 2. Major Classes of Nuclear Wastes

Type	Source
1. High-Level Wastes	Spent fuel assemblies Wastes generated by reprocessing spent fuel
2. Transuranic Wastes (>10 nc/gram transuranic material)	Spent Fuel Reprocessing Plutonium fabrication Operations
3. Low-Level Wastes (<10 nc/gram transuranic material)	Reactor Operation Fuel Fabrication
4. Uranium Mine and Mill Tailings	Uranium mining operations
5. Gaseous Effluents	Reactor operation Fuel reprocessing

The quantities of these wastes that exist at the present time are summarized in Table 3.(3) The quantities are broken down, where applicable according to whether they originated from commercial power generation or defense operations.

TABLE 3. Quantities of Existing Wastes (1977)

Type	Quantity
High-Level Waste, Reprocessed:	
Commercial	80,000 ft^3
Defense	9,400,000 ft^3
High-Level Waste, Spent Fuel from Commercial Power Generation	2,300,000 kilograms
Transuranic Waste: (Contained TRU)	
Commercial	123 kilograms
Defense	1,100 kilograms
Low-Level Waste:	
Commercial	15,800,000 ft^3
Defense	50,800,000 ft^3
Uranium Mill Tailing	1.27×10^8 metric tons

Of these waste classes, high-level wastes and transuranic wastes are being considered for deep geologic storage. To put into perspective the time that these wastes are hazardous relative to other commonly handled substances, Figure 1 shows a toxicity curve for spent fuel and wastes derived from processed spent fuel.(3,4) The toxicity of the ores assumes that they are of the same volume as the total volume of the waste repository. Within the 1,000 to 10,000-year time frame, the reprocessed wastes fall below the toxicity index for a 0.2% uranium ore body whose volume is equal to the needed repository. Figure 2 shows how these time frames compare to times of social or geological significance.(5)

With this introduction to nuclear wastes, quantities, and times needed for reduction to relatively low toxicity levels, we need to look at a hypothetical repository to gain insight into assessing waste form performance. Figure 3 shows such a hypothetical repository where the waste is interred in a rock unit impervious to associated aquifer formations.

To assess the performance of a given waste form and surrounding barriers, water is assumed to penetrate into the formation containing the repository. Other studies are presently underway to address the probability and consequences of possible repository disruptive events. Although it is believed to have a low probability, we will consider the case where an uplifting rock unit disrupts the repository allowing flowing water to contact the waste package. Figure 4 shows the disrupted repository along with aquifer flow to a well which could provide a path for radionuclides released from the waste form to contact the biosphere.

Figure 5 depicts the components of the repository that are available for interacting with the waste form. Water penetrating to the waste form will have an altered chemical composition because of interaction with the host rock, backfill, engineered barriers, and canister material in the presence of thermal and radiation fields. The waste form will now alter chemically with respect to this fluid composition as illustrated by Figure 6. After a solution has reached the waste form, several reaction zones will be established as a function of distance from the waste form as follows:

1. Waste form - canister - solution alteration, waste form dominate.
2. Waste fluid - engineered barrier reactions, engineered barrier dominates.
3. Waste fluid - engineered barrier - host rock interactions, host rock dominates.
4. Waste fluid - host rock reactions away from engineered barriers, but still under the influence of temperature and radiation fields.
5. Waste fluid - multiple rock media interactions at ambient temperature and away from radiation fields.

Since the radiation and temperature fields decrease with time, the chemical interactions are dependent upon when water penetrates the waste form-barrier system. Other disruptive events to a repository, such as a fault, could cause failure of the engineered barriers and exposure of the bare waste to a flowing solution. This "open" system allows for different types of reactions than the more "closed" type of system mentioned previously. Both systems need to be studied for assessing waste form performance.

From this discussion of potential waste form, barrier and host rock interaction, we can draw up a list of primary reactions governing the release of radionuclides from the waste form-barrier system. This radionuclide "source term" then provides input to radionuclide transport studies.

The reactions of major importance that will influence the nuclide flux available for migration from the near-field are:

1. Diffusion of radionuclides from the waste form matrix.
2. Chemical alteration of waste form matrix to new minerals and/or solids containing radioisotopes.
3. Waste induced chemical alteration of engineered burning, backfill, and host rock.
4. Precipitation reactions keyed to solubility limits of waste elements.
5. Oxidation - reduction reactions.
6. Sorption - desorption reactions.

The major parameters involved are:

1. Temperature.
2. Solution composition.
3. Solution flow rate.
4. Type of waste form and surrounding barriers.
5. pH.
6. Oxidation - reduction state.
7. Radiation field.
8. Pressure (in maintaining liquid H_2O at repository temperatures).

These reactions and parameters involved in radionuclide release create a complicated system to study. As part of the Waste Isolation Safety Assessment Program at PNL, sponsored by the Office of Nuclear Waste Isolation for the Department of Energy, we are approaching the problem in stages of increasing compexity.

These stages are briefly outlined as follows:

1. Waste-solution interactions, laboratory scale.
2. Waste + engineered barriers + host rock interactions, laboratory and intermediate scale.
3. Verification of laboratory and intermediate scale tests via full-scale hot cell or in-situ tests.

In the first part of our studies we have started experiments to determine radionuclide release rates from bare waste forms in contact with simulated groundwater solutions and sorption reactions between radionuclides and host rocks without radiation and thermal fields.

Table 4 outlines the waste forms and conditions being examined in this phase of experiments.

The second phase work has started and is being accelerated. Our first tests combine the waste form, a failed canister, host rock and simulated groundwater. Subsequent studies will add engineered barriers. The same detailed analyses will be performed as shown in Table 4. We feel the third phase is very important and preliminary input is being compiled to identify the approach to be taken.[6,7]

Common to all the work outlined in these phases of waste performance tests is the development of a model to describe the release of radionuclides from the waste form. Figure 7 outlines this development. The first model will be a mathematical expression based on previous and ongoing work on waste form solution interactions. As much mechanistic understandings as possible will be added as more detailed surface and solution analyses are completed. The model will be expanded to account for more complex interactions expected in Phase II work. Phase III will verify the laboratory scale based model on a full scale system.

Some general comments should be made at this time concerning preliminary results from Phase I studies outlined earlier. These are summarized here:

- Radionuclide leach rates drop by a factor of 10 in the first ~20 days of

TABLE 4. Waste Performance Studies: Phase I, Waste-Solution Interactions

- Waste Forms

High-Level Waste:	Spent fuel Glass
Transuranic Waste:	Glass Concrete Polymers Urea - Formaldehyde Bitumen

- Variables

  Time
  Temperature
  Solution composition
  Solution flow rate
  Radiation field
  Oxidation potential

- Analysis

Solution	Radioisotopes Matrix elements Valence state Chemical species
Surface and solid state analysis on waste forms and alteration products	Elemental profile Metallography x-ray diffraction SEM/microprobe ESCA SIMS

- Refined Output

  Data bank
  Release model based on empirical data and mechanistic understanding.

solution contact and then tend to level off, as shown in Figure 8 for ^{239}Pu. The leach test used is based on the IAEA procedure.(8)

- Spent fuel and glass have similar leach rates initially with spent fuel tending toward congrument dissolution whereas glass does not. Figure 9 depicts the leach rates from spent fuel of radionuclides released into WIPP "B" Salt Brine by the IAEA test. Figure 10 shows similar information for fully radioactive waste glass in deionized water using the same test procedure.(9)
- Flow rate effects on radionuclide release are dependent upon temperature, having negligible impact at 25°C and increasing release an order of magnitude at 75°C as indicated in Figure 11.
- Solution compositions ranging from deionized water to saturated salt brine causes an order of magnitude difference in leach rate. Deionized water and simulated bicarbonate groundwater give the highest leach rates. Figure 8 illustrates this for ^{239}Pu release.
- Leach rate is a very strong function of temperature and follows an Arrhenius relationship. Leach rates for glass appear to approximately double with an increase of 10°C over a range of 25°C to 300°C.(11) Figure 12 depicts this trend, which is the same seen for the continuous flow test in Figure 11.

Other studies (High-Level Waste Immobilization Program, PNL) have undertaken to evaluate effects of self-radiation and thermal treatment, showing -

- There is no significant change in leach rate as a result of alpha-decay damage in waste glasses. Figure 13 shows leach rate data taken as a function of radiation dose for nitreous and denutrified glass. The changes are insignificant whether based on weight loss or ^{244}Cm solution analysis.(12) The difference between Cm based and weight loss leach rates is likely due to the strong pH dependence for Cm solubility.

- Heat treatment causing partial crystallization of waste glasses has a small effect on leach rate. Figure 14 compares relative leach rates of four glasses before and after devitrification. The leach rates are clearly much more dependent on composition than on state of devitrification. For the elements shown, glass 76-68 actually has smaller losses in the devitrified form.(13)

Besides identifying the types of basic research needed to assess waste form performance and radionuclide sorpotion and to understand the controlling processes, we must consider the short term engineering needs. The following questions must be answered to evaluate the engineering design of the waste package system and to assess repository safety.

1. The characteristics of the release radionuclide flux,
    a) Types and amounts of radionuclides.
    b) Valence state.
    c) Radionuclide solution species.
    d) Sorption properties of repository and associated geologic media.
2. The mechaisms (diffusion, corrosion, surface precipitation, re-crystallization) of alteration of the waste form,
    a) By an "open" system in which other barriers have minimal interaction; a fracture flow environment.
    b) By a "closed" system where low solution flow rates allow maximum interaction and formation of new mineral systems.
3. Evaluation of alteration products formed,
    a) Thermodynamic stability with respect to the repository.
    b) Effects of long term radiation damage and transmutation.
    c) Kinetic behavior.

This level of effort of scientific understanding should make it possible to optimize waste form-barrier combinations for a given geologic media and assess the safety of that choice.

Summary

The development of an adequate data base for assessing the safety of geologic nuclear waste disposal is a vital part of the repository licensing process. Although programs are underway to obtain this information, several research areas must be advanced to maximize interpretation of ongoing experiments in a timely fashion. The major areas needed are:

> Waste form and engineered barrier/rock media surface analysis techniques to study structure and composition changes when subjected to anticipated repository conditions.
>
> Trace level radionuclide chemical species and valence state detection in low and high ionic strength solutions.

In addressing the area of basic research needs, caution must be exercised to pay close attention to the needs of radionuclide release modelers and repository design engineers. This is essential so that the direction of basic research and subsequent data collection is responsive to repository licensing needs.

References

1. Report to the President by the Interagency Review Group on Nuclear Waste Management, TID-28817, Draft, October, 1978.
2. Report to the President by the Interagency Review Group on Nuclear Waste Management, TID-29442, March, 1979.
3. Tonnessen, K. A., J. J. Cohen, "Survey of Naturally Occurring Hazardous Materials in Deep Geologic Formations: A perspective on the Relative Hazard of Deep Burial of Nuclear Wastes," UCRL-52199, January, 1977.
4. Haug, H. O., Some Aspects of Long Term Problems of High-Level and Actinide-Contaminated Spent Fuel Reprocessing Wastes from the U-Pu and Th-U Fuel Cycles, IAEA-SM-207/51, 1976.
5. Malaro, J. C., "High-Level Nuclear Waste Management in the United States: A Time for Decisions," Nuclear Safety, vol. 19, No. 3, May-June, 1978.
6. National Waste Terminal Storage In-Situ Demonstration Workshop, August 29-30, 1978, at the Office of Nuclear Waste Isolation, Columbus, Ohio.
7. "Earth Science Technical Plan for Mined Geologic Disposal of Radioactive Waste" by the Office of Nuclear Waste Management, U.S. Department of Energy, U.S. Geologic Survey, and U.S. Department of the Interior, TID-29018, Draft, January, 1979.
8. Hespe, E. D. ed., "Leach Testing of Immobilized Radioactive Waste Solids, A Proposal for a Standard Method", Atomic Energy Review, 9:1, 1971.
9. Bradley, D. J., "Leaching of Fully Radioactive High Level Waste Glass", PNL-2644, Pacific Northwest Laboratories, Richland, Washington 99352, September 1978.

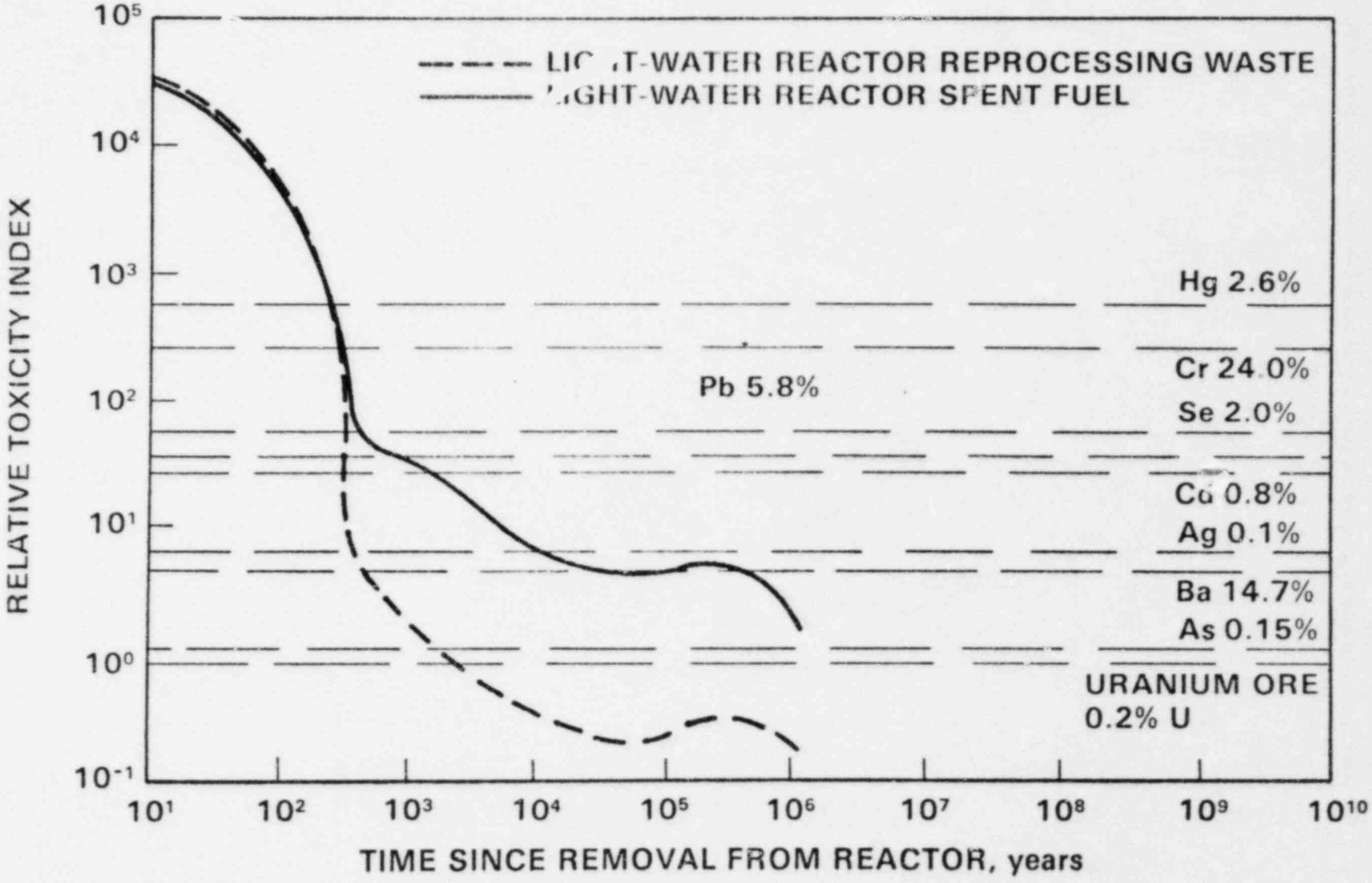
10. Weed, H. C., D. G. Coles, D. J. Bradley, R. W. Mensing, and J. W. Schweiger, "Leaching Characteristics of Actinides from Simulated Reactor Waste Glass", UCRL-81147, Rev. 1, January 18, 1979.

11. Westsik, J. W., Turcotte, R. P., "Hydrothermal Reactions of Nuclear Waste Solids, A Preliminary Study", PNL-2759, Pacific Northwest Laboratories, Richland, Washington 99352, September 1978.

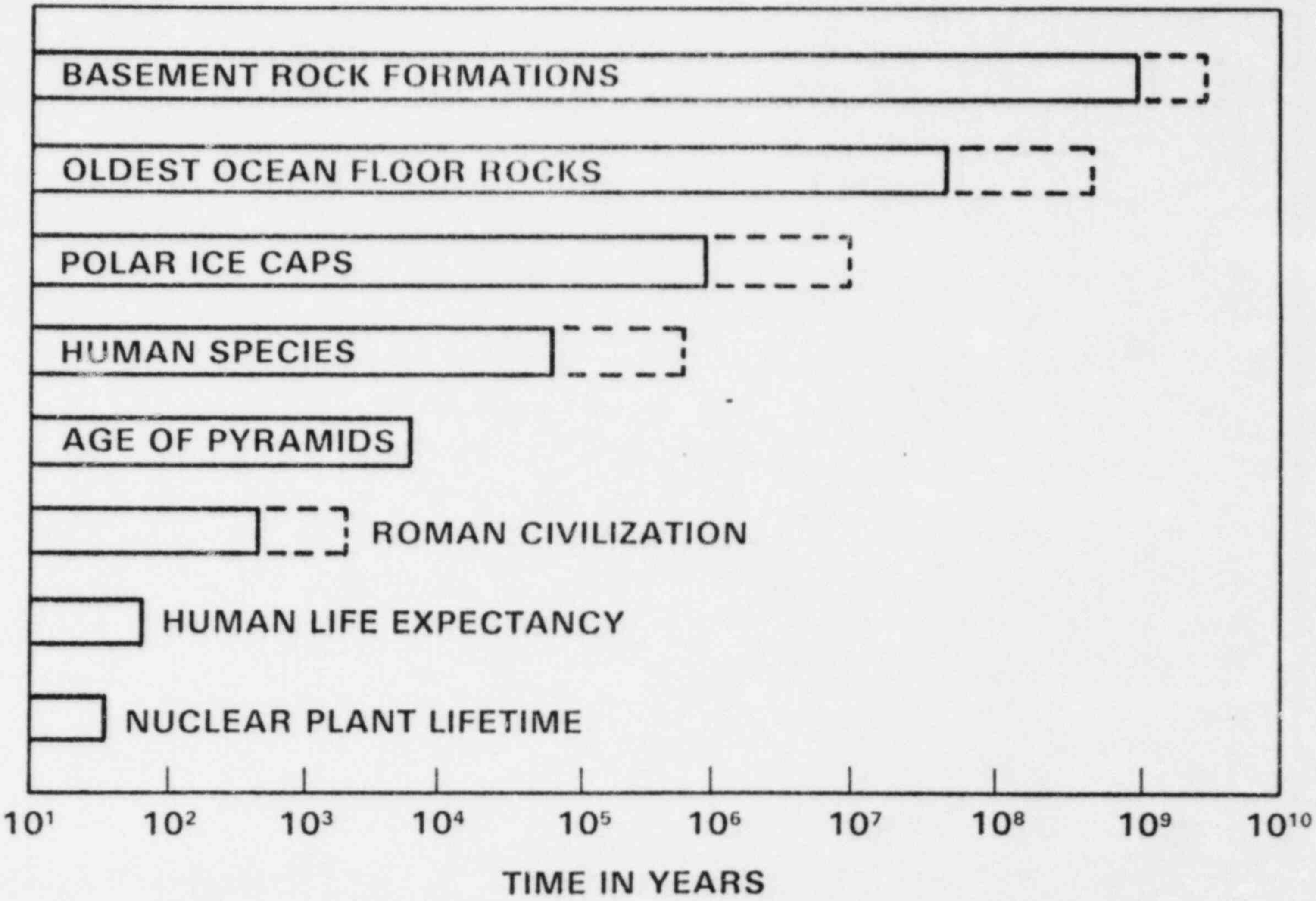
12. Weber, W. J., Turcotte, R. P., Bunnell, L. R., Roberts, F. P. and Westsik, J. H., Jr., "Radiation Effects in Vitreous and Devitrified Simulated Waste Glass", PNL-SA-7327, Pacific Northwest Laboratories, Richland, Washington 99352, May 1979.

13. Walk, J. W., and Westsik, J. H., Jr. "Devitrification and Leaching Effects in the HLW Glass - Comparison of Simulated and Fully Radioactive Waste Glass, PNL-SA-7326, Pacific Northwest Laboratories, Richland, Washington 99352, May 1979.

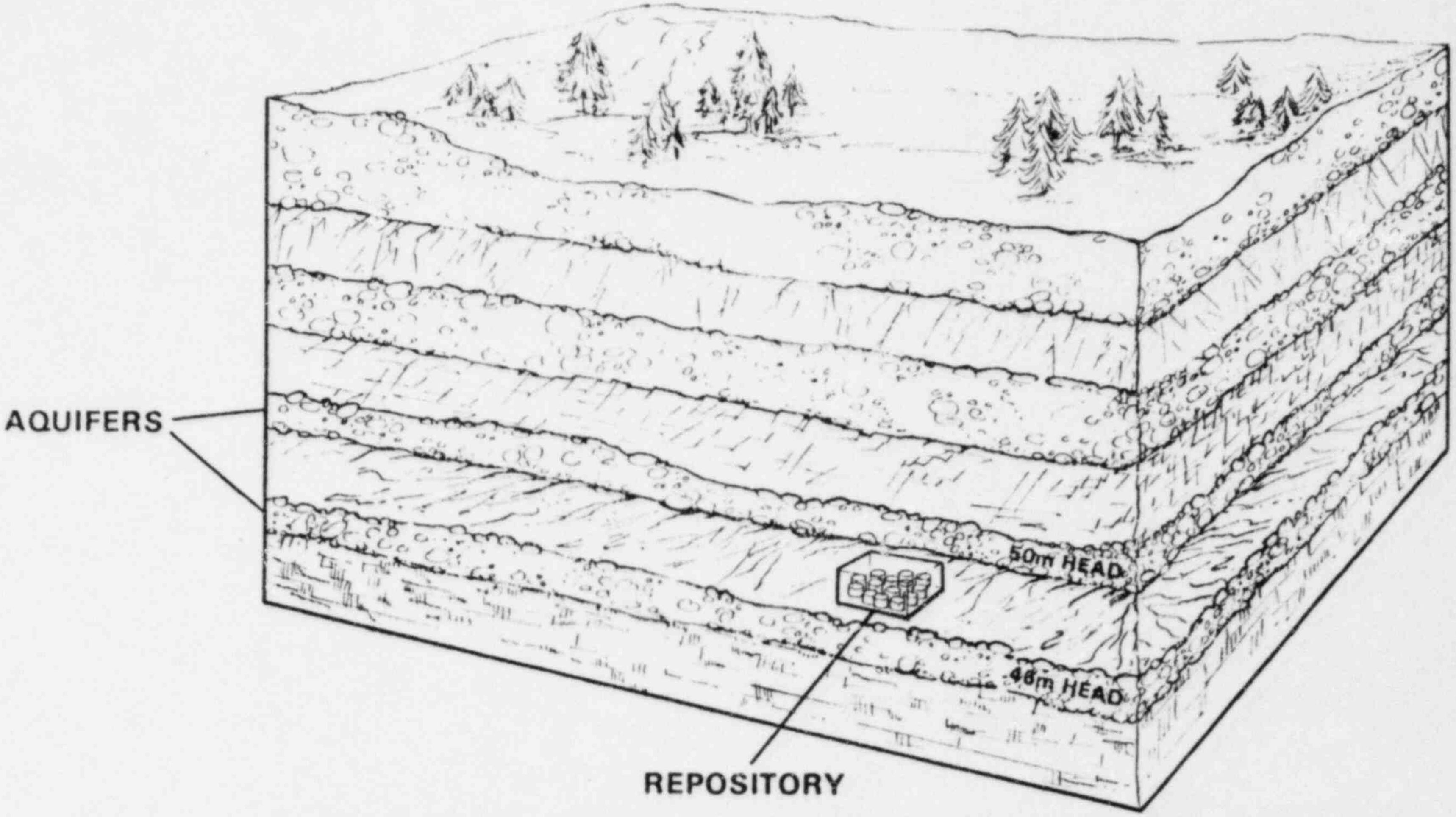
TOXICITY OF NUCLEAR WASTE REPOSITORY OVER TIME (RELATIVE TO THAT OF EQUAL VOLUMES OF AVERAGE MINERAL ORES OF TOXIC ELEMENTS



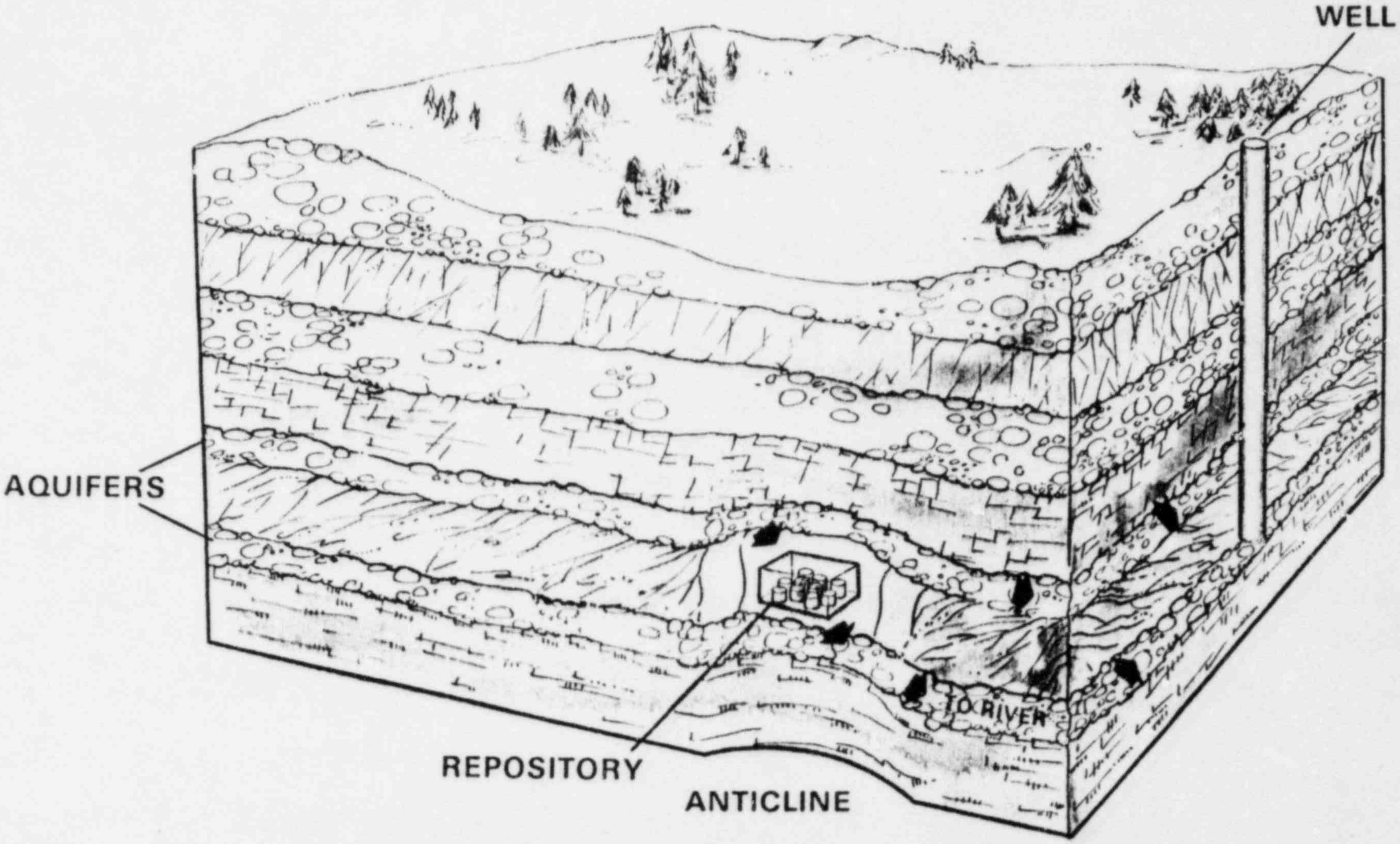
TIMES OF SOCIAL OR GEOLOGIC SIGNIFICANCE



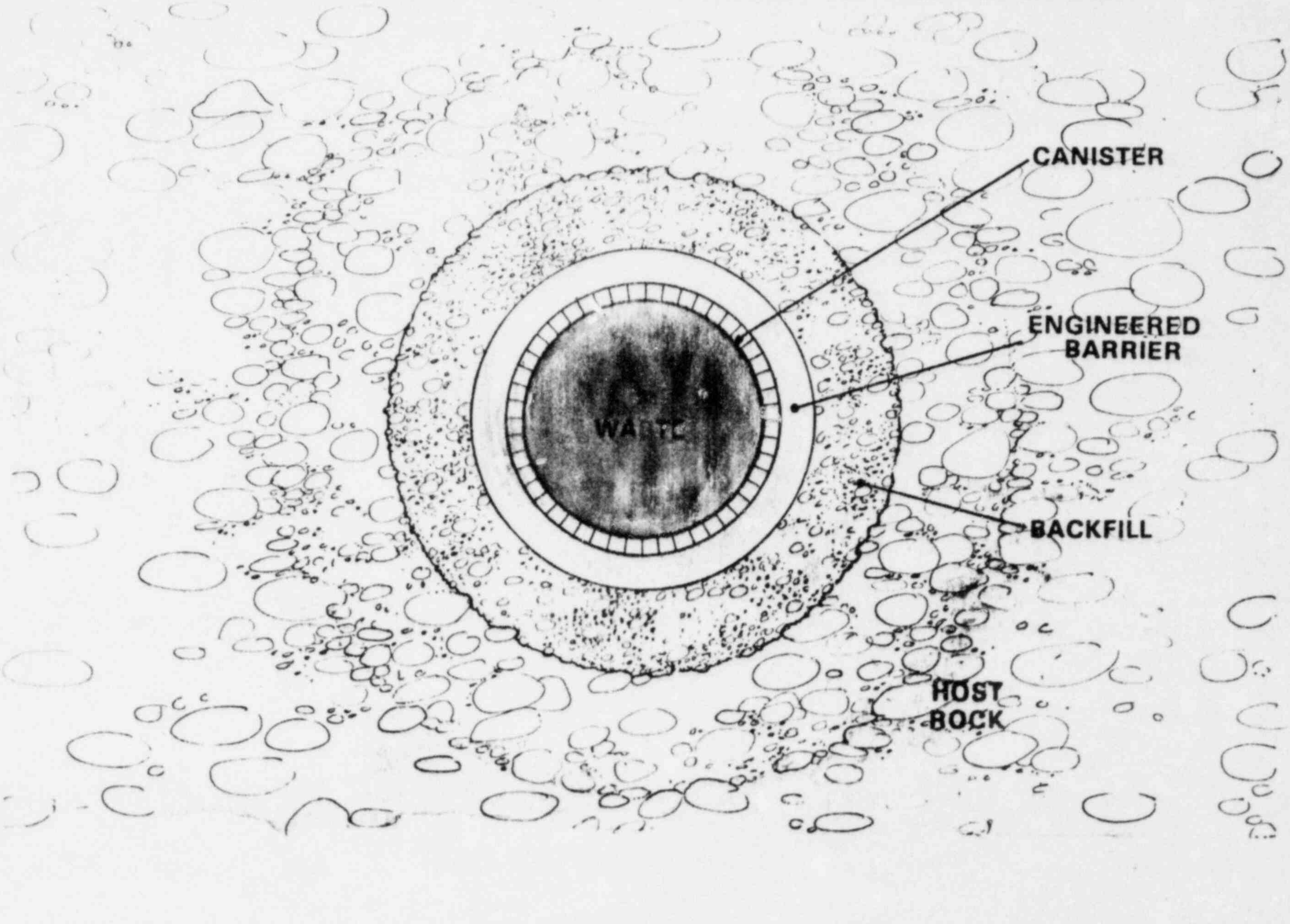
INTACT REPOSITORY



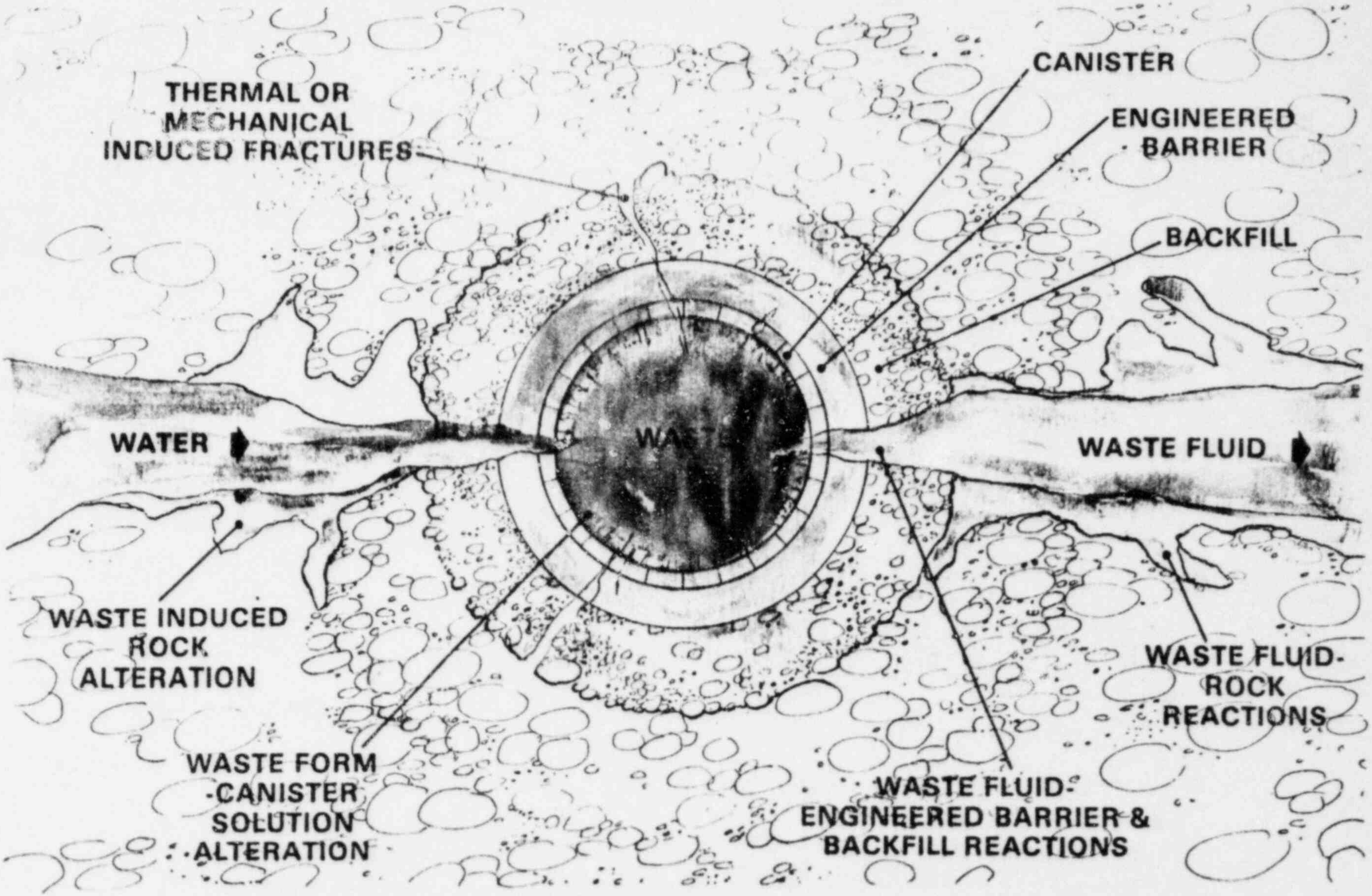
BREACHED REPOSITORY



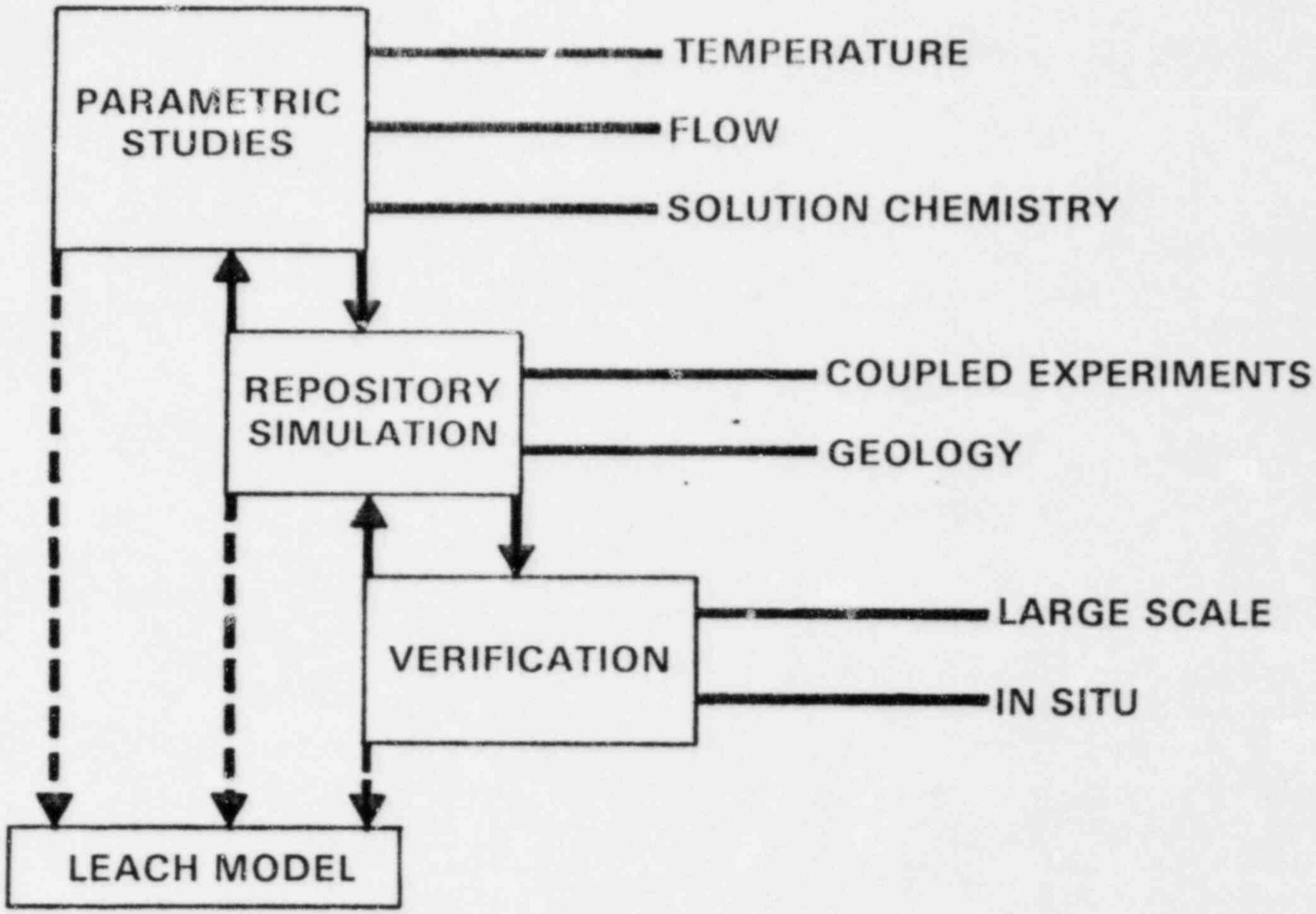
COMPONENTS OF WASTE INTERACTION SYSTEM



WASTE INTERACTIONS



LEACH MODEL DEVELOPMENT



PARAMETRIC STUDIES

TEMPERATURE

FLOW

SOLUTION CHEMISTRY

REPOSITORY SIMULATION

COUPLED EXPERIMENTS

GEOLOGY

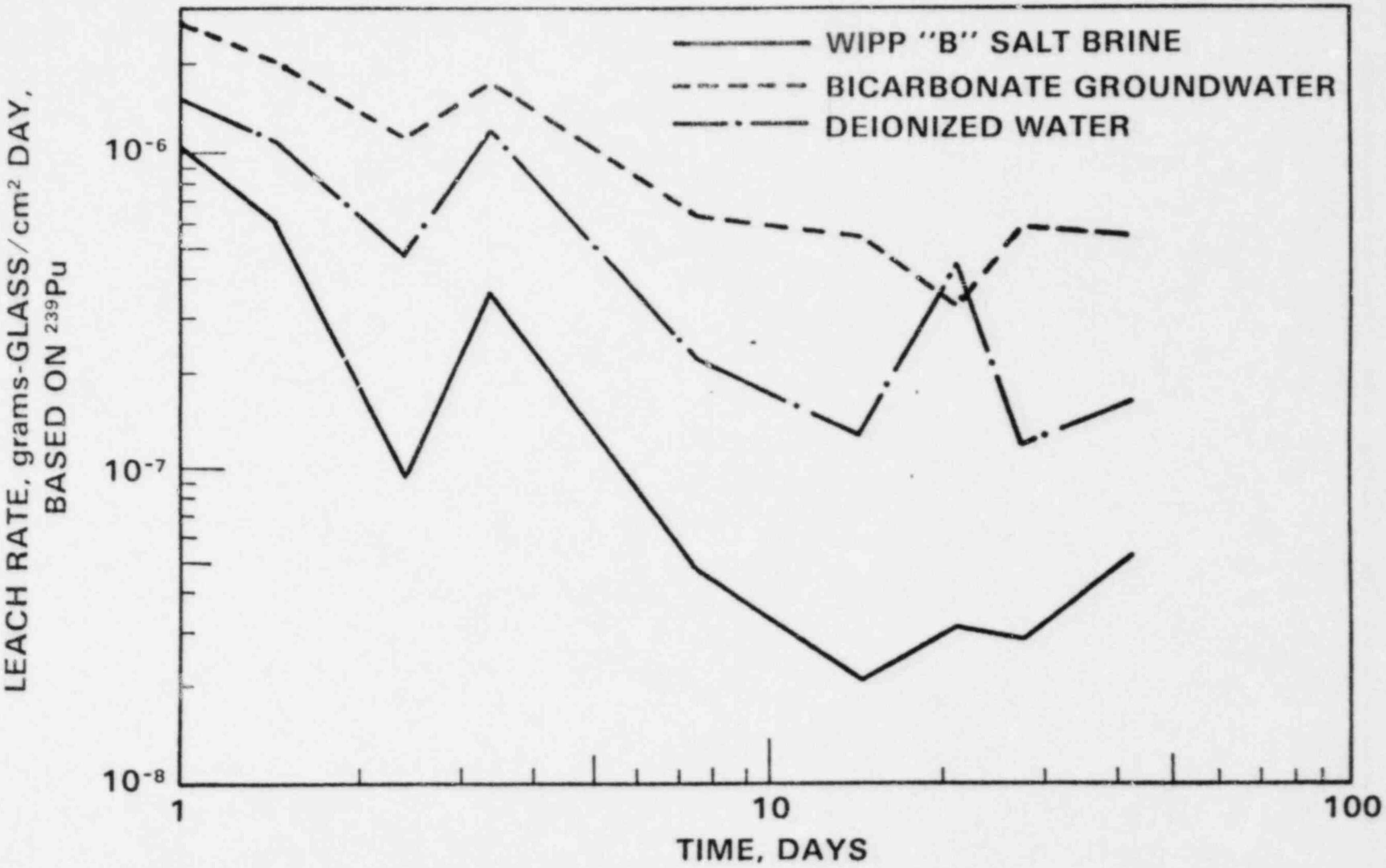
VERIFICATION

LARGE SCALE

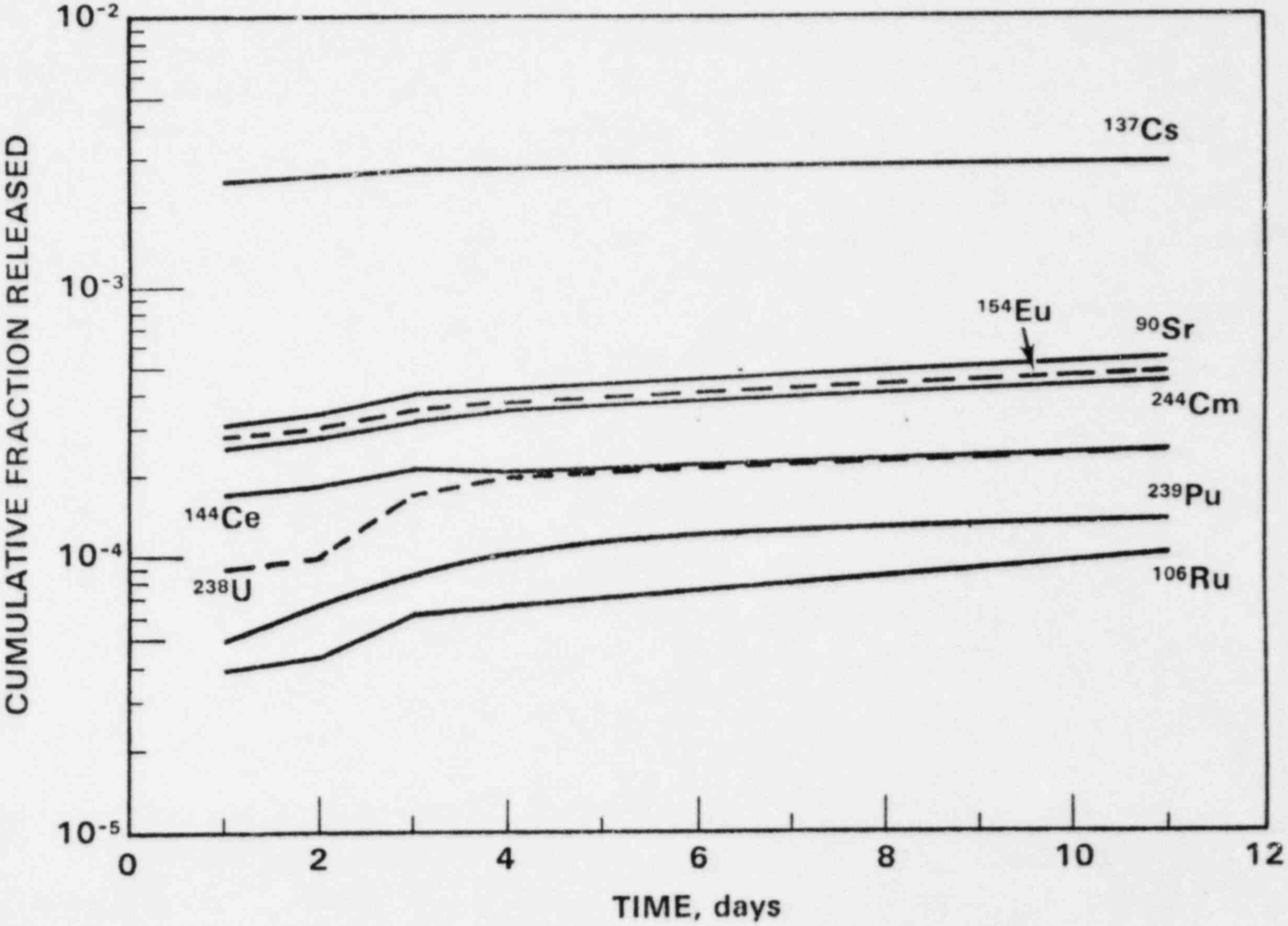
IN SITU

LEACH MODEL

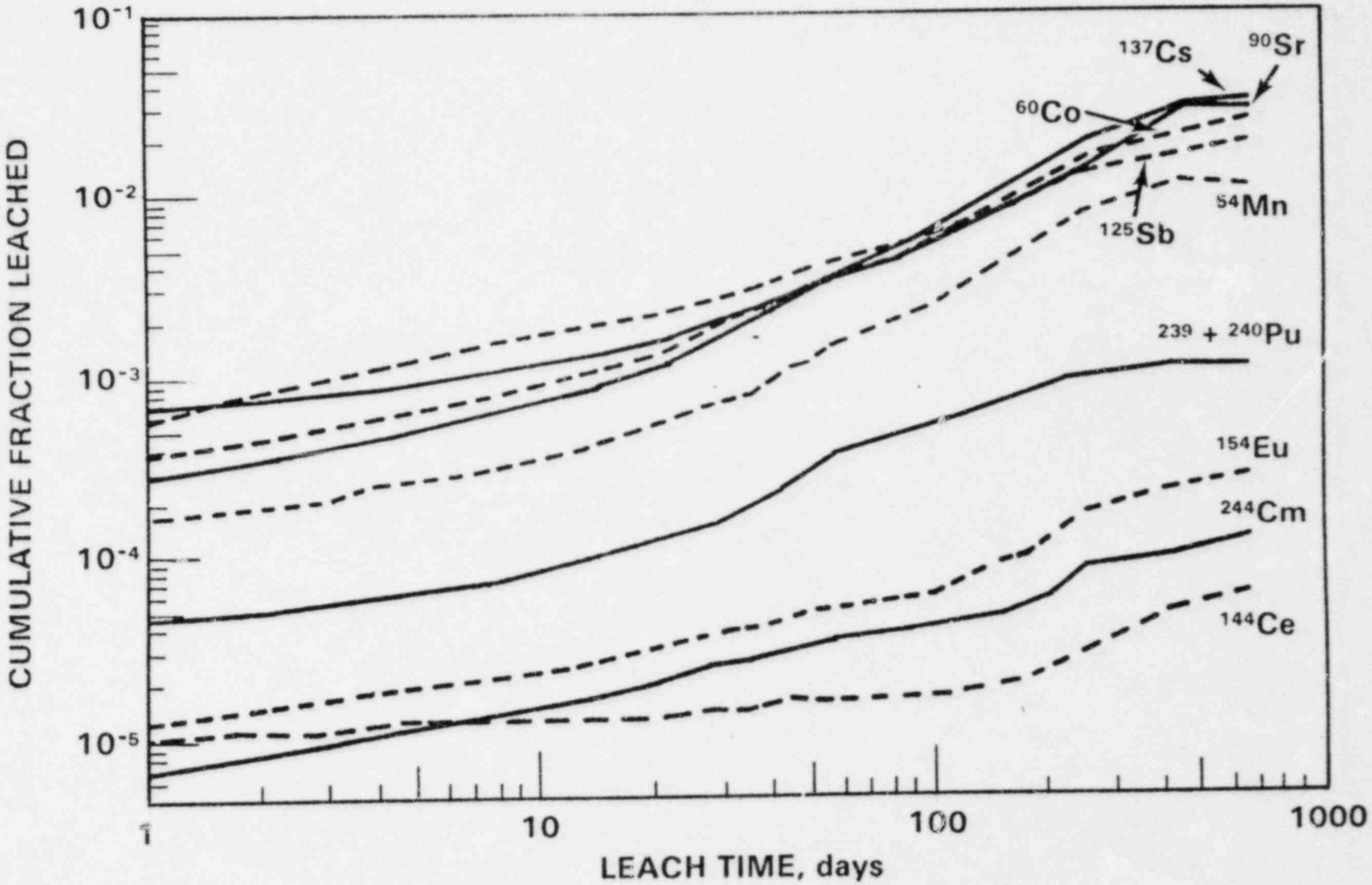
IAEA LEACH TEST SIMULATED WASTE GLASS (76-68)
(T = 25°C)



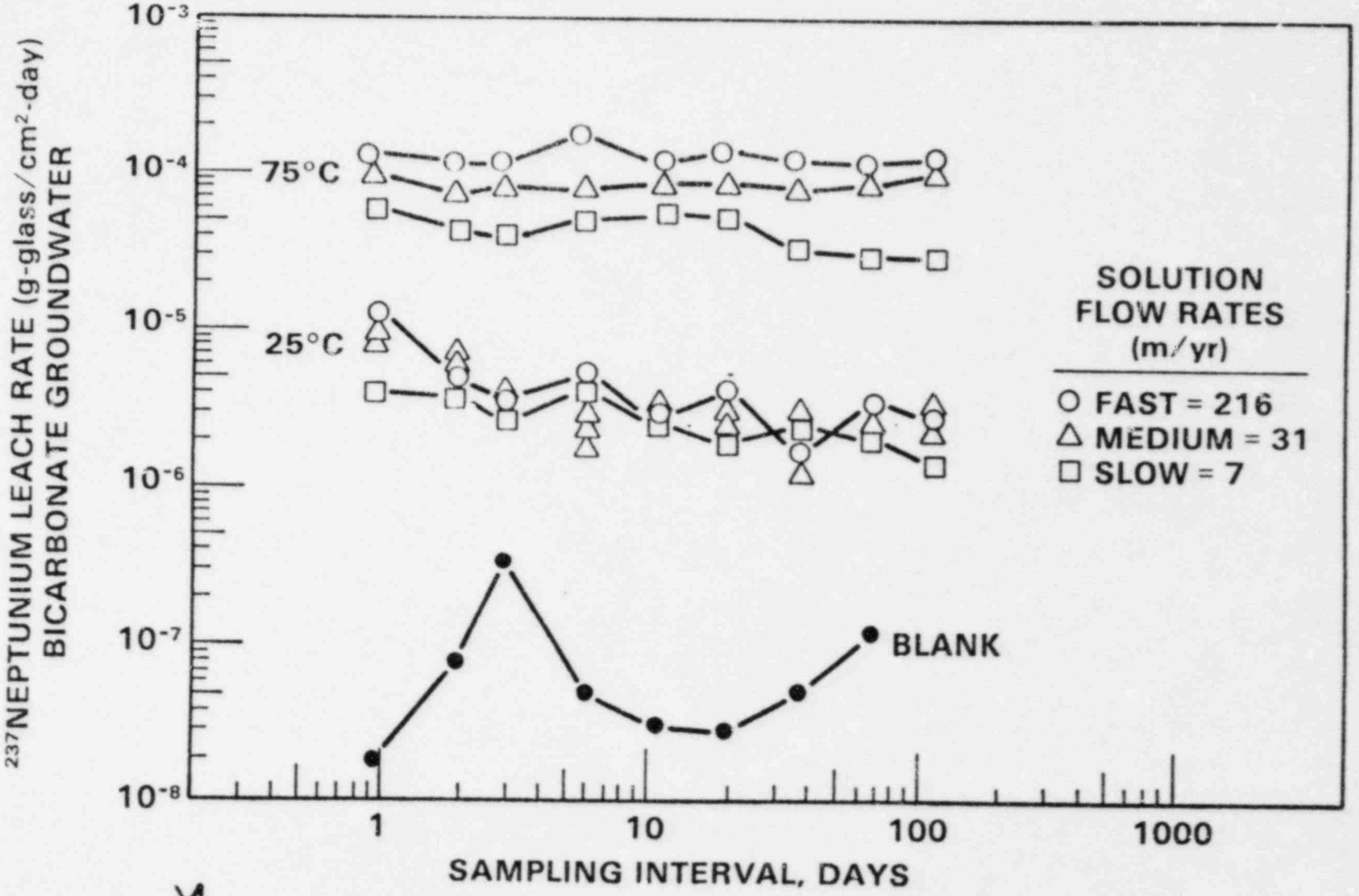
SPENT FUEL, IAEA LEACH TEST
WIPP "B" SALT BRINE, T = 25°C



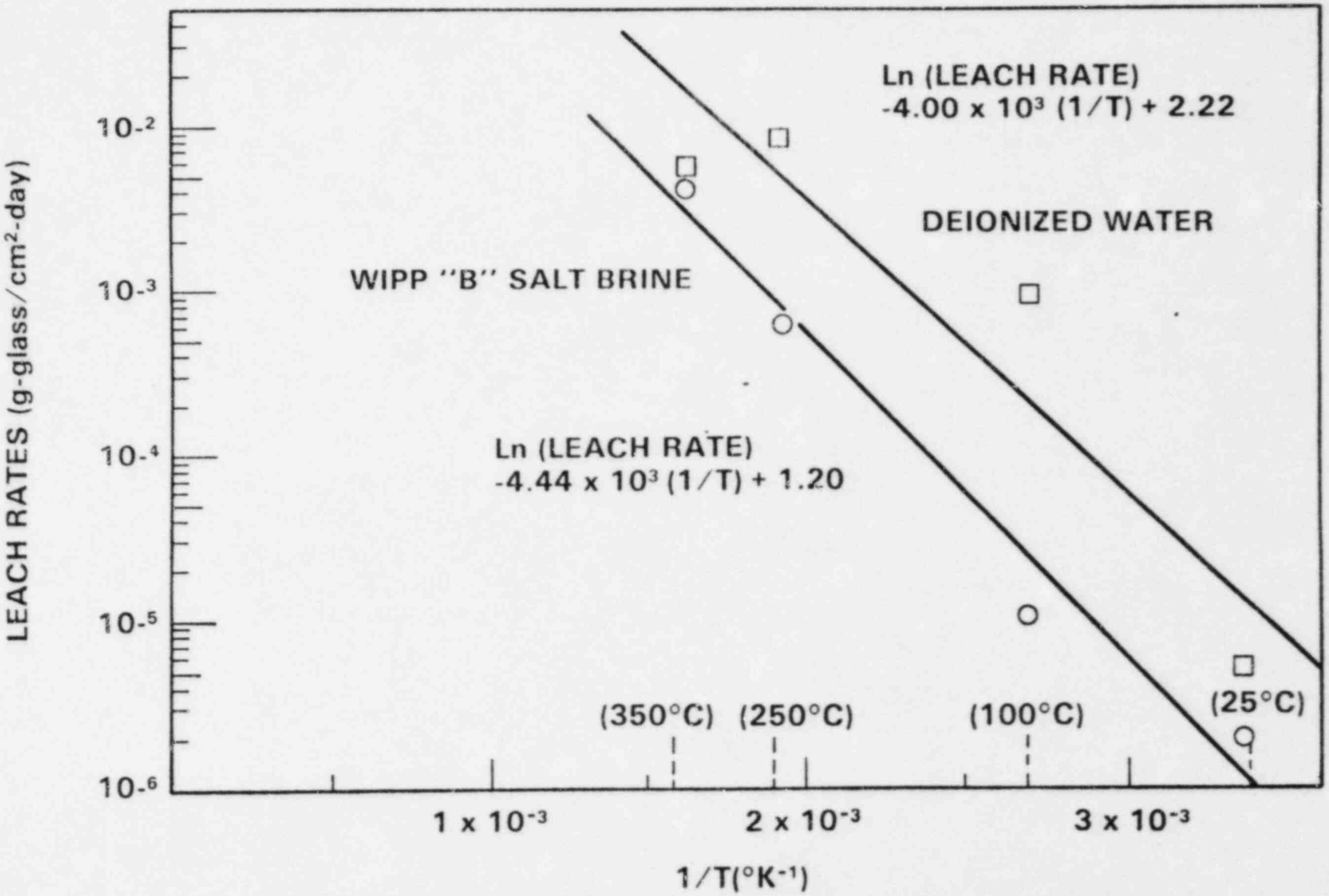
FULLY RADIOACTIVE WASTE GLASS (72-68)
IAEA LEACH TEST
DEIONIZED WATER (T = 25°C)



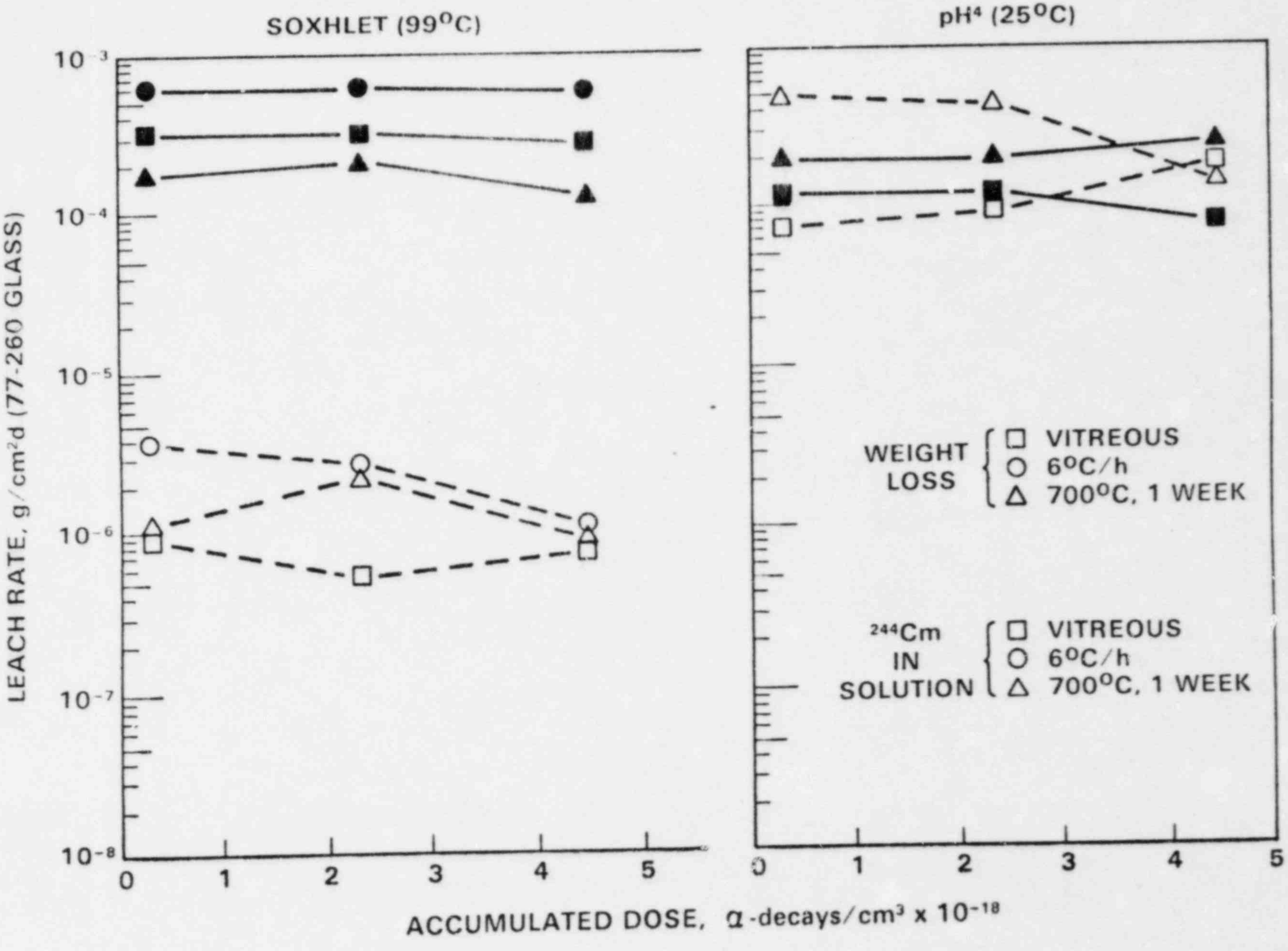
CONTINUOUS FLOW LEACH TEST—76-68 GLASS
BICARBONATE SOLUTION (.03 M)



EFFECT OF TEMPERATURE ON 76-68 WASTE GLASS LEACH RATES



EFFECT OF ALPHA PARTICLE DOSE ON WASTE GLASS LEACH RATES



RELATIVE RELEASES OF ELEMENTS FROM NON-RADIOACTIVE GLASSES (1 WEEK, 75°C) NORMALIZED TO THE FRACTION OF SODIUM RELEASED FROM AS-PREPARED 72-68 GLASS